

ABSTRACT

The ground - state structures and binding energies of the metal cations to dipyrromethene (DIPY) based ligands are determined using density functional theory (DFT) methods. Two lanthanide metal cations in their +3 oxidation states are examined including: Gd³⁺ and Eu³⁺. Calculations at B3LYP, BHandHLYP, and M06 levels of theory using 6 - 31G* and 6 - 311+G(2d,2p) basis sets are employed to determine the structures and theoretical estimates for the binding energies of the structurally modified complexes. Structures of the Gd - based complexes are compared to those of the Eu - based complexes to further assess the electronic effects on the binding energies. Also the optical and redox properties of the structurally modified DIPY will be investigated. In addition to theoretical studies, the effects of structural variations of DIPY on their photocytotoxicity in terms of photophysical properties and in vitro and in vivo efficacies are determined. Synthesis of DIPY based structures with different functionalities is carried out in order to improve hydrophilicity of the current structures. Synthesis of DIPY based structures with extended conjugation at the pyrrolic position is performed in order to prepare photosensitizers that absorb in the longer wavelengths. Such complexes may be activated deeper in the tissues and may therefore be clinically favored. The photodynamic therapy (PDT) efficacy of the DIPY - based photosensitizers is tested on a panel of leukemia and solid tumor cell lines, with particular attention on their 56 2015 Arusha, Tanzania structure - activity relationships. The PDT efficacy of the gadolinium based DIPYs currently prepared is compared to the ones in the market