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DFT CALCULATIONS OF SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF DONOR-ACCEPTOR SUBSTITUTED NICKEL(II) SCHIFF BASE COMPLEXES

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There is considerable interest in new highly efficient nonlinear optical (NLO) materials due to their potential applications in optoelectronic and photonic technologies. In recent years, various donor(D)-π-acceptor(A) type organometallic and inorganic compounds have been studied extensively for their NLO activity. Amongst them, dipolar D/A substituted Schiff base complexes and metal alkynyl complexes have received special attention. Despite the strong interest in the NLO properties of these systems, there are limited studies on the NLO properties of metal alkynyl Schiff base hybrids. The effects of different donor and acceptor substituents and diamine bridges on the second order NLO properties of metal salen and salphen complexes are also less explored. The present work reports density functional theory (DFT) and time dependent (TD) DFT calculations of second order NLO properties of a series of D/A substituted Ni(II) Schiff base complexes at the B3LYP/6-31G(d)/LanL2DZ level of theory, including a novel Ru alkynyl Schiff base hybrid complex. Incorporating a strongly electron donating Ru alkynyl fragment into an unsymmetrical A-substituted Schiff base platform is anticipated to result in a significant nonlinear optical (NLO) response due to synergistic effects. Calculations showed that all the Ni(II) Schiff base complexes have a planar Ni-salen core, resulting in a significantly high total static first hyperpolarizability (β_{tot}) compared to their free Schiff bases. The presence of D- and/or A-groups on the salicylidene groups results in a reasonable increase in the β_{tot} value. The salphen complex bearing D = $N(CH_3)_2$ donor and A = NO_2 showed the lowest HOMO-LUMO energy gap, and therefore it shows the highest β_{tot} value. The diagonal β_{zzz} component is the dominant β tensor for all the D/A complexes, with the quadratic NLO character of these systems being one-dimensional. The D-A complex based on 2,3-diaminomaleonitrile showed the highest β_{tot} value between the complexes with different diamine bridges due to the presence of electron withdrawing CN groups, which lowers the HOMO-LUMO energy gap considerably. The introduction of the electron donating Ru alkynyl fragment into the nitro-substituted Ni(II) Schiff base unit with diaminomaleonitrile bridge resulted in a marked increase in the computed β_{tot} value, higher than those of the complexes with organic donors. The calculations also showed that the second order NLO properties of the hybrids are sensitive to the nature of the co-ligands around Ru. Based on the TD-DFT studies, the hybrid complexes show a substantially red-shifted metal to ligand charge transfer band, which may be responsible for their large calculated NLO coefficients.

Keywords: DFT, First hyperpolarizability, Metal alkynyl complexes, Nonlinear optics, Schiff base complexes