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Article

Correlation between Second Ionization Potential and Nonlinear Optical Properties of Bivalent Transition-Metal Complexes: A Quantum Chemical Study

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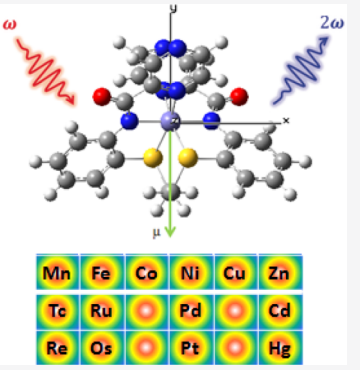
ABSTRACT: Discovering new materials with excellent nonlinear optical responses has recently become a very interesting research topic in the different domains of materials science. Currently, density functional theory (DFT) has been shown to be a powerful tool in the explanation and prediction of the performance of novel nonlinear optical (NLO) materials. Quantum chemical calculations using DFT/TD-DFT with the B3LYP exchange−correlation functional are reported to study the NLO properties of 26 bivalent transition-metal (TM) complexed by six acyclic hexadentate ligands providing pyridyl/pyrazine−amide-thioether/ether coordination and differing by the nature of the methylene dichalcogenate spacer between the rings. However, the geometry parameters and the theoretically predicted UV−vis absorption spectra of the optimized compounds M(II)L^{i} are in excellent agreement with the experiment, when available, the trends among the nature of the TM, the importance of the ligand spacer, and of the substituents of the pyridine/pyrazine amide ligand are discussed. To the best of our knowledge, our work evidences for the first time that the hyper-polarizability, second harmonic generation, and hyper-Rayleigh scattering response of TM coordination complexes can be correlated to the second ionization potential of metal and spin state of complexes.



1. INTRODUCTION

Currently, the discovery of new nonlinear optical (NLO) materials has become one of the major challenging research fields because of its potential applications in various fields such as photonics, opto-electronics, optical communications, optical switching, optical computing, optical memory, dynamic holography photodynamic therapy, and biological imaging.[1−4]

Among systems, metal complexes with π-conjugated ligands have emerged and grown as a respectable class of NLO materials,[5−8] owing to their thermal stability, redox switching ability, and ultrafast response times.[9] Also, the metal complexes display a large variety of molecular geometry and electronic properties by virtue of the coordinated metal center. Furthermore, metal complexes have several additional electronic properties that distinguish them from organic compounds due to their low-energy charge-transfer transitions such as the ligand to metal charge transfer (LMCT), metal to ligand charge transfer (MLCT), and intra-metal charge transfer (IMCT) electronic transition. On the other hand, to provide a high NLO response, the coordination complex with the π-conjugated ligand should be asymmetric, and it should possess low-energy absorption with charge-transfer transitions, whereas the difference between the excited-state and the ground-state dipole moment should be large.[5]

The bonding model of transition-metal (TM) complexes can explain many important properties of the TM complexes including their magnetism, structures, stability, oxidation state, reactivity, and optical (linear and nonlinear) properties. It is to be noted that in the TM complexes, the energies of the five (n − 1) d orbitals of the TM ion are affected by the nature of the ligands (strong or weak field).

In the case of TM complexes in octahedral geometry, the $d_{x^2-y^2}$ and d_{z^2} orbitals interact very strongly with the ligands and form new σ bonding and antibonding molecular orbitals, called the "e_g" set of orbitals, in Oh symmetry. On the other hand, the d_{xy}, d_{xz}, and d_{yz} orbitals interact less strongly with the donor ligands and develop π orbitals (bonding and antibonding interactions), called the "t_{2g}" set of orbitals. The filling of these e_g and t_{2g} orbitals depends on the ligand field, leading to the spin state of the complex. For the weak field, we have the high spin (HS) state, with a filling of, successively, the t_{2g} (α spin), the e_g (α spin), the t_{2g} (β spin), and the e_g (β spin). For the strong field, we have low spin (LS) state with successively filling the t_{2g} (α spin), the t2g (β spin), the e_g (α spin), and the e_g (β spin). Therefore, in the case of $3d^4$−$3d^7$ configurations (Scheme 1), the occupation of the e_g orbital preferentially to a

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