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DFT/TD-DFT investigation of linear and nonlinear optical properties of porphyrin-bridged push-pull ruthenium complexes

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There is considerable interest in nonlinear optical (NLO) materials based on transition metal complexes due to their potential in a broad range of technological applications such as photonics, optical computing, and signal processing. For the past two decades, various metal complexes have been studied for their large NLO response, amongst which metal alkynyl complexes and push-pull metalloporphyrins have received special attention. The present study proposes a new class of NLO-active metal complexes which features a highly polarizable metalloporphyrin component, a ruthenium alkynyl complex that serves as an electron donor and a tricyanofuran (TCF) electron acceptor. Computational studies employing density functional theory (DFT) and time-dependent (TD) DFT were undertaken to explore the linear optical and second-order nonlinear optical properties of these hybrid species. The calculated first hyperpolarizabilities of proposed chromophores are considerably larger than those of their phenylene counterpart with the porphyrin-bridged Ru complex containing the thiophene-TCF acceptor displaying the largest first hyperpolarizability value. The calculations also showed that the calculated NLO coefficients of ruthenium complexes are reasonably larger than those of their organic counterparts and that the composition of the porphyrin unit has a reasonable effect on the NLO properties. The calculated electronic spectra of these species feature a significantly red-shifted charge transfer band in the visible region compared to corresponding spectra of their phenylene analogues. This band arises mainly due to the transition from HOMO to LUMO and may be responsible for the large NLO response predicted for the porphyrin-bridged Ru complexes studied herein.

Keywords: *Nonlinear Optics, computational chemistry, Porphyrin, organometallics*

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