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Quadratic nonlinear optical properties of photochromic DTE–containing ruthenium complexes: A DFT study

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Interest in molecular switches has grown enormously in recent years due to their applications in current and prospective fabrication of smart soft materials and photonics technologies. A variety of organic and metal-containing molecular systems capable of switching quadratic and cubic nonlinear optical (NLO) properties has been investigated, but most of the reported compounds are restricted to switching between three states at most. In this study, multi-stimuli (photochemical, protic, electrochemical) switching of quadratic NLO properties of a ruthenium alkynyl complex containing a photochemically-active dithienylperfluorocyclopentene (DTE) bridge trans-$[Cl(dppm)_2Ru(C{\equiv}C\text{-}1\text{-}C_6H_4\text{-}4\text{-}C{\equiv}C\text{-}DTE\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4\text{-}1\text{-}NO_2)]$ afforded six stable and independently addressable states that have been studied systematically using density functional theory (CAM-B3LYP/6-311G(d)/SDD(Ru)). The calculations showed that, for the Ru(II) complexes, the photo-induced ring-closing reaction leads to a substantial increase in the NLO response, with the ring-closed forms exhibiting a better π-conjugation between the electron donor and electron acceptor substituents compared to their ring-opened analogues. On the basis of time-dependent (TD) DFT calculations, the lowest-energy charge transfer band is considerably red-shifted upon ring-closure, making a significant contribution to the total quadratic NLO response. Protonation of the alkynyl complexes to afford vinylidene complexes results in a reduction in the computed NLO response. This may be due to NLO-inefficient intraligand transitions dominating in the low-energy region of the optical spectra of vinylidenes. One-electron oxidation gives rise to a significant increase in the quadratic NLO data, the significantly red-shifted absorption bands in the electronic spectra of the oxidized forms appearing to favor large NLO responses. Each of the six stable stimuli-accessible species has distinct quadratic NLO responses, and with each pathway interconverting two of the species affording a possible binary (photochemical, protic or electrochemical) switch.

Keywords: Molecular switches, Nonlinear optics, Organometallics, Computational chemistry

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