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FIRST HYPERPOLARIZABILITIES AND EXCITATION ENERGIES OF PORPHYRIN-BRIDGED RUTHENIUM COMPLEXES FEATURING NITROPHENYL ACCEPTOR: A DFT STUDY

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The search for highly efficient nonlinear optical (NLO) materials has been accelerated in the past two decades due to their many potential applications, such as switching and optical signal processing. In the present study, density functional theory (DFT) and time-dependent DFT (TDDFT) calculations of a new family of nonlinear optical (NLO) metal complexes featuring both $[Ru(C{\equiv}CC_6H_4\text{-})Cl(H_2PCH_2CH_2PH_2)_2]$ electron-donating and nitrophenyl electron-withdrawing groups fused to a porphyrin core via ethynyl or alkenyl linkers are reported. The calculated static first hyperpolarizabilities (β) and low-lying linear optical data of these novel porphyrin-bridged Ru complexes were compared with those of ruthenium analogues with phenylene based bridges. The calculations showed that the porphyrin complexes show superior optical nonlinearity than the corresponding phenylene Ru complexes. The donor-bridge-acceptor structure leads to a significant increase in the calculated β, as expected. However, bridge lengthening by adding a phenyleneethynylene unit leads to a decrease in the static β value. Varying the bridge composition by replacement of the ethynyl linkages by an alkenyl group appears to have a reasonable impact on the optical nonlinearity for both structures. For the porphyrins, the hyperpolarizability decreased on replacing the yne linkage between the porphyrin unit and nitrophenyl acceptor by the *E*-ene group. For the acceptor containing porphyrins, the simulated UV/Vis spectrum features a significantly red-shifted Q band and an intense, high-energy B band, whilst calculations predict an intense optical band in the region of 350 nm – 450 nm for the Ru complexes with phenylene based bridges. For all the donor-bridge-acceptor Ru systems, the molecular orbital analysis revealed that the low-energy band shows substantial donor-acceptor charge-transfer character, thus making a significant contribution to the first hyperpolarizability β. The HOMO and LUMO energy gaps of the porphyrins are smaller than those of the Ru complexes with phenylene based bridges. As a result, the low-energy Q band (which results from the LUMO to HOMO) in the former is significantly red-shifted, which may explain the disparity in their β values.

Keywords: Computational chemistry, Metal alkynyls, Nonlinear optics, Porphyrins