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COMPUTATIONAL STUDY OF LINEAR AND NON-LINEAR OPTICAL PROPERTIES IN NOVEL HEPTAZINE DERIVATIVES

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The development of advanced optoelectronic and photonic technologies is critically dependent on the discovery of new materials with superior non-linear optical (NLO) properties. Heptazine, a highly efficient electron acceptor having a planar conjugated structure, presents a promising core structure for octupolar D_3A-type NLO systems. Symmetrical substitution of peripheral hydrogens by electron-donating groups considerably enhances the NLO response. Notably, organometallic s-hepatazine systems display exceptional multi-photon absorption activity. Surprisingly, there have been no experimental or theoretical second-order NLO studies on these organometallic heptazine derivatives. This study employed density functional theory (DFT) and time-dependent DFT (TD-DFT) at the CAM-B3LYP/6-31+G(d)/SDD level of theory, selected after testing various methods and basis sets, and led to results consistent with previously reported work. This approach was applied to explore novel heptazine derivatives bearing amino (NH_2) and dimethylamino [$N(CH_3)_2$] donor groups, and nitro (NO_2) acceptors, substituted at the 2,5, and 8 positions of the heptazine ring, either directly or indirectly attached, through linkers such as $–C_6H_4–$ and $–C_6H_4–C{\equiv}C–C_6H_4–$. Instead of organic donor groups, the $Ru(dHpe)_2Cl$ unit was attached to the heptazine core in organometallic systems. Extending the π-conjugation in donor-substituted derivatives results in an increase in the first, second and third-order polarisabilities due to improved electron delocalisation, while the NO_2-substituted heptazine analogues show lower values. The replacement of the organic donor groups by the organometallic unit leads to a significant increase in the first and second-order polarisabilities. Natural bond orbital analysis confirms that the donor groups increase the negative charge on the core, enhancing delocalisation and polarisability. The efficacy of s-heptazine as the core structure was investigated for organometallic molecules. Heptazine derivatives showed the largest NLO coefficients compared to triazine and commonly used benzene core geometries. The lower HOMO-LUMO energy gap in heptazine can be attributed to this prediction. Based on the TDDFT calculations, 2,5,8-tri(donor)-s-heptazines show red-shifted bands. When NO_2 groups are substituted, the low-energy band is blue-shifted. Moreover, Ru complexes enhance NLO via metal-to-ligand charge transfer, with heptazine giving the highest response. Building on this, future work may explore frequency-dependent NLO behavior and conformational effects on organometallic systems.

Keywords: DFT, First hyperpolarisability, Heptazine, Metal alkynyls, Nonlinear optics