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Computational protocols for studying Pt(II) complexes: Applications in Photonics and Pt-195 NMR spectroscopy

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There is great interest in platinum (Pt) chemistry due to its wide range of applications, such as the development of technological materials[1] and drugs with biological potential[2]. However, computational studies of Pt complexes are costly and difficult to resolve[3]. Thus, it is necessary to develop suitable methodologies for the prediction of properties such as electronic, nonlinear optical and NMR spectroscopic properties. In the present study, we proposed computational protocols for studying electronic properties, first hyperpolarizability (β) and the Pt-195 NMR chemical shift (δ^{195}Pt) in Pt(II) complexes with potential application in dye-sensitized solar cell (DSSC), nonlinear optics (NLO) and anticancer drugs. All Pt(II) complexes in the present study had their structures optimized at B3LYP/LANL2TZ(f)/def2-SVP/IEF-PCM(UFF) level – Gaussian 16 Rev. C.01 program. Regarding the δ^{195}Pt, a set of 30 Pt(II) complexes with experimental data available in the literature were selected. Initially, computational protocols at GIAO-DFT-Functional/NMR-ZORA/CPCM level, considering 39 functionals were considered for cisplatin and carboplatin. After, the best computational protocols were applied for all selected 30 Pt(II) complexes. The protocol GIAO-BP86-SC-ZORA/NMR-ZORA/CPCM presented the best description of δ^{195}Pt with a mean relative deviation (MRD) of only 4.5% in relation to the experimental data and a coefficient of determination (R^2) of 0.9853. Subsequently, this computational protocol is being evaluated in the characterization of inclusion complexes between Pt(II) complexes and β-cyclodextrin. Regarding the first hyperpolarizability (β), the N^C^N-1,3-bis[5-(trifluoromethyl)pyridin-2-yl]-4,6-difluorobenzene platinum(II) p-dimethylaminophenylacetylide complex, which experimental $\mu\beta_{EFISH}$ (1907 nm) value is -2020 x 10^{-48} esu, was selected. Computational protocols considering a set of 38 DFT functionals, 10 platinum basis sets, and 13 ligands basis sets were proposed in Gaussian 16 Rev. C.01 program. From the calculated results, the best protocol, B3LYP/LANL2TZ(f)/NLO-III[4]/IEF-PCM(UFF), presented a relative deviation (RD) in relation to the experimental value of only 0.9%. The results showed that a specific NLO basis sets are interesting for predicting the β. Subsequently, a broader set of Pt(II) complexes is being evaluated. Finally, the electronic properties of Pt(II) complexes selected will be evaluated with a view to their applications as DSSC.

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