

Investigation of the Excited States and Intramolecular Charge-Transfer Transitions in Porphyrin-Based Nanostructures

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Porphyrins have attracted research interest for many years due to their relevance in biology, catalysis and medicine. The application of functional dyes relies on their optoelectronic properties, and the accurate prediction of excited states in such systems is important for design of new synthetic porphyrins with desirable optical properties. Our study provided a significant improvement in accuracy of the agreement between theoretical prediction and experiment of the localized $\pi-\pi^*$ and intramolecular charge transfer (ICT) transitions, thus allowing confident interpretation of UV-vis-NIR spectra.

For fully conjugated oligoporphyrins (see Fig. 1a), a systematic red-shift in the near-infrared absorption has been demonstrated which can potentially be used in photodynamic therapy (PDT) against cancer. These oligomers have three optical windows: the lowest energy near-infrared or infrared transition region (I), the low energy visible range transition region (II) and the transition region (III) located on the edge of the ultraviolet zone. Therefore, the accurate assignment and theoretical prediction of the major optical transitions is important in order to identify the features of these absorption bands for molecular electronics and biomedical applications.

Recently, it was shown that for a large variety of phthalocyanines and their analogues, the time-dependent density functional theory (TDDFT)-predicted energies of the Q_x - and Q_y -bands and their splitting correlate well with the amount of Hartree-Fock exchange present in the specific exchange-correlation functional (ECF), with the LC-BP86 and LC-wPBE ECFs providing the best agreement between theory and experiment (<0.05 eV). The pure GGA (BP86) exchange-correlation functional severely underestimated, while long-range corrected LC-BP86 and LC-wPBE ECFs strongly overestimated, the intramolecular charge-transfer (ICT) transitions experimentally observed in the 450–650 nm region for the-OR, -SR, and -NR₂substituted phthalocyanines and their analogues. Hybrid CAM-B3LYP/PCM, PBE1PBE/PCM, and B3LYP/PCM ECFs were found to be much better in predicting the energies of such ICT transitions. Moreover, a single exchange-correlation functional was not found that could accurately predict the energies and the splitting of the Q_x - and Q_y -bands as well as the energies of ICT transitions [1].

Based on previous results, our current investigation showed a good agreement between theory and experiment with respect to the transition

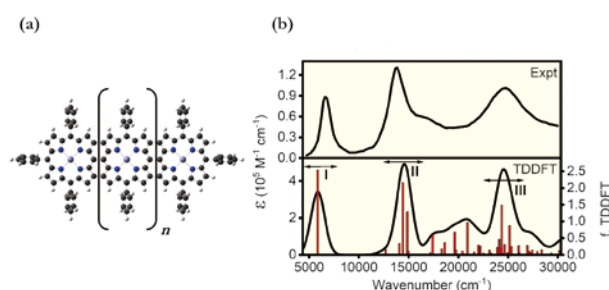


Fig. 1 (a) Structure porphyrin tapes ($n=1-10$); (b) experimental and TDDFT-predicted UV-vis spectrum of tetramer.

energies and intensities (Fig. 1b).

This afforded band assignments which are more reliable than anything reported previously. It was confirmed that with increasing size of the porphyrin tape, there was an increase in ICT states between spectral regions II and I. Moreover, the spectral region III was dominated by a single transition state that originated almost exclusively from a HOMO to LUMO excitation. A quantitative correlation was shown between the x-polarized Soret-type transition and the most intense band that was experimentally observed in region II [2]. We also demonstrated, at least for the shorter tapes (**2-4**), that spectral region I was dominated by the y-polarized Soret-type transition, as shown in Fig. 1b. In the cases of porphyrins **1-12**, our calculations agreed well with the semi-empirical ZINDO/S spectral predictions and available experimental MCD data reported previously. In particular TDDFT-based sum-over-states calculations correctly predicted the signs of the MCD A- and B-terms in the Q-band region.

References

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- [2] R. V. Belosludov, D. Nevenon and V. N. Nemykin, *J. Phys. Chem. A*, **125**, 2480 (2021).

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