Density functional calculations on the optical absorption spectrum of a porphyrin derivative.

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Dyads containing 3,4-dimethyl-N-{2-[10,15,20-tris-(3,5-di-tert-butyl-phenyl)-porphyrin-5-yl]-phenyl}-benzamide (H_2P–O34)[1] as an electron donating unit have been found to be involved in photochemically induced electron transfer processes. In this work, the absorption spectrum of H_2P–O34 has been determined by means of density functional method. The calculations were performed at the generalized gradient approximation (GGA) level, using the Perdew-Wang exchange-correlation functional[2] with a numerical basis set including polarization functions and numerical integrations, as implemented in the Dmol3 software.[3]
The optimized geometry of the H_2P–O34 molecule has been calculated and the structural details will be reported. The energy eigenvalues and symmetries for all HOMO and for the frontier LUMO orbitals in the ground state have been analyzed. In addition, the energy differences between some excited states and the ground state have been calculated. The geometry of the ground state was used in the excited state calculations, but the orbitals were allowed to relax.
The calculated absorptions will be compared with the experimental data. Absorption measurements are currently carried out at the Institute of Materials Chemistry. The wavelengths evaluated from the excited state calculations by computing the energy differences between the excited states and the ground state will be compared with the results obtained directly from the ground state HOMO – LUMO calculations as well as with the experimental data. On the basis of the results calculated in this work it is expected that DFT methods can be successfully applied to the study of the electron transfer processes within dyad molecules.

References

(1) Imahori H., Hagiwara K., Aoki M., Akiyama T., Taniguchi S., Okada T., Shirakawa M., Sakata Y., *J. Am. Chem. Soc.* **1996,** *118*, 11771.

(2) Perdew J. P., Chevary J. A., Vosko S. H., Jackson K. A., Pederson M. R., Singh D. J., Fiolhais C., *Phys. Rev. B*, **1992**, *46*, 6671.

(3) Computational results were obtained using software programs from MSI. The calculations were done by Dmol3® program and the graphical displays were printed out from the Cerius2® molecular modeling system.