THESIS

THEORETICAL AND SPECTROSCOPIC INVESTIGATION ON THE CONDUCTING POLYMER IN THE CLASS OF CARBAZOLE DERIVATIVES

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Doctor of Philosophy (Chemistry)
Graduate School, Kasetsart University
2006

ISBN 974-16-2955-9

Songwut Suramitr 2006: Theoretical and Spectroscopic Investigation on the
Conducting Polymer in the Class of Carbazole Derivatives. Doctor of Philosophy
(Chemistry), Major Field: Chemistry, Department of Chemistry.
Thesis Advisor: Associate Professor Supa Hannongbua, Dr.rer.nat. 235 pages.
ISBN 974-16-2955-9

The torsional potential energy surfaces of conducting polymer in the class of carbazole derivatives were carried out by *ab initio* (HF and MP2) and density functional theory (B3LYP and BH&HLYP) calculations with several basis sets. The torsional potentials were fitted to a six-term truncated Fourier expansion for validity the methods and basis sets. The results show that the exchange-correlation (B3LYP and BH&HLYP) effects of density functional theory tend to systematically decrease the relative torsional energies. The ground state geometries from BH&HLYP calculations can provide relatively accurate predictions of vertical excitation energies better than that of obtained from B3LYP geometries. This can suggest that the Fourier least-squares-fitted method is appropriate for method validation. The vertical excitation energies were calculated by the time-dependent density functional theory using BLYP, BP86, BH&HLYP, PBE1PBE and B3LYP functional with the 6-311++G(2d,2p) basis set based on B3LYP/6-311G(d,p) optimized geometries. From the results, TD-PBE1PBE and TD-B3LYP methods predict the excitation energies for Cz-dimer, Cz-co-Fl and Cz-co-Th (3.84, 3.83 and 3.89 eV, respectively) in good agreement with experimental data (3.85, 3.83 and 3.84 eV, respectively). An analysis of the vertical singlet-singlet transition was also performed and the results indicated that for Cz-dimer, Cz-co-Fl and Cz-co-F, S_1 transition plays an important role, whereas the S_2 is important for Cz-co-P and Cz-co-Th. Excitation to the S_1 and S_2 states corresponds almost exclusively to the promotion of an electron from the HOMO to LUMO. In Cz-co-F, this transition is unstable due to low oscillator strength. The structural geometries of ground and excited state were performed by the B3LYP and TD-B3LYP, respectively, using several density functional theories with the SVP and TZVP basis sets. The geometry of excited state was found to be more planar than ground state. Absorption and emission energies from the relaxed excited states were obtained from TDDFT calculations performed on the S_1 optimized geometries and excellent agree well with experimental data.

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ACKNOWLEDGEMENTS

I wish to express my deep gratitude to a number of persons who giving me guidance, help and support to reach my goal of this thesis. First of all, most of credits in this thesis should justifiably go to my advisor, Associate Professor Dr. Supa Hannongbua, for her valuable guidance, continuous support, kindness and encouragement throughout the course of my graduate. I am deeply appreciated to Professor Dr. Peter Wolschann who always provides me for considerably helpful comments and discussion on various aspects to my work. I am grateful and special thanks to Professor Dr. Professor Dr. Alfred Karpfen for valuable guidance and assistance in suggestion the problems and offers me a grant from the ÖAD for partial support within the Asea-Unet. Furthermore, I would like to thank my committees, Professor Dr. Peter Wolschann, Associate Professor Cholticha Noomhorm and Assistant Professor Toemsak Srikhirin for their helpful comments and suggestions.

The Royal Golden Jubilee Ph.D. Program (3C.KU/46/B.1) and Kasetsart University are grateful acknowledged for some financial supports for my Ph.D. study and for partial support via Grant-in-Aid for thesis. The Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (ADB-MUA), and Laboratory for Computational and Applied Chemistry (LCAC), Center of Nanotechnology, Kasetsart University and are grateful acknowledged for research facilities. Generous supply of computing time and research facilities by the ZID of the University of Vienna are gratefully acknowledged when I did the research at Institute for Theoretical Chemistry and Structure Biology, University of Vienna, Austria. In addition, Kasetsart University Research and Development Institute (KURDI) are also acknowledged for some financial support.

Finally, I would like to express my most profound gratitude to my parents, my sister and my brother, who sustained and encouraged me throughout my educations.

Songwut Suramitr
October, 2006