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# Quantum-Chemical Studies on Porphyrins, Fullerenes and Carbon Nanostructures

 Springer

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# Abbreviations

BDE	Bond dissociation energy
BSSE	Basis superposition error
CMO	Canonical molecular orbital
CPU	Central processing unit
CDA	Charge decomposition analysis
ECP	Effective core potential
EM	Elongation method
H <sub>2</sub> TPP	Free base tetraphenyl porphion
HOMO	Highest occupied molecular orbital
HFC	Hyperfine coupling
LRC	Long-range corrected
LUMO	Lowest occupied molecular orbital
NLO	Nonlinear optics
NR	Nuclear relaxation
OLED	Organic light-emitting diode
$O(N)$	Linear scaling
OTE	Oligo(2,5-thienylene-ethynylene)
QR	Quadratic response
QFMM	Quantum fast multipole method
RLMO	Region localized molecular orbital
SOC	Spin-orbit coupling
SSC	Spin-spin coupling
SW-BN/CNT	Single wall boron nitride/carbon nanotube
TD DFT	Time-dependent density functional theory
TPA	Two-photon absorption
ZFS	Zero-field splitting



# Abstract

This book contains a theoretical study of electronic structure, optical and spectroscopic properties of a number of compounds, in particular, porphyrins, fullerenes, and carbon nanostructures, which include heteroatom single wall nanotubes and others. The milestone of the book is to study the nonlinear optical properties and disclose the influence of the nature of substitutes to enhance nonlinear optical effects. The book presents qualitatively new results that address the issue that is of practical importance—namely, the discovery and development of materials for photosensitizers, organic LEDs, and solar cells. The performed analysis of a wide range of quantum-chemical methods aimed to study photophysical properties of porphyrin and fullerene derivatives. In particular, as a result of the work it was found the cause and relationship between the overshooted values of polarization components of the electron and the donor ability of the substitute. The electronic and vibrational contributions to the hyperpolarization of fullerene-chromophore donor–acceptor pairs are qualitatively and quantitatively evaluated. Single and two-photon absorption spectra of functionalized fullerene derivatives that were calculated on the basis of quantum-chemical calculations agree well with experimental results obtained by MALDI-TOF-MS, ATR-IR, UV, NMR, Z-scan spectroscopies. Particular attention is paid to the design and development of new  $(O)N$  linear scaling methods for application in quantum-chemical theory of electronic structure. As shown in the book these methods display accuracy comparable to the accuracy of traditional method calculations; moreover, they are greatly reducing cost of CPU time, which make them an indispensable tool for studying the electronic structure of nano sized compounds.

# Introduction

*Actuality of the topic:* The current importance of the work is in urgent need to use energy-saving technologies—namely, the creation of highly efficient materials for energy conversion of sunlight with a high quantum yield, photosensitizers, photoconductors, devices based on organic light-emitting diodes in computer and telecommunication networks. Most current methods for quantum-chemical calculations that can be applied to polyatomic systems have a whole series of approximations, which cannot preserve the high quality of results. However, for numerical integration, which is used to study NLO must have accuracy in the values of total energies at least up to the tenth decimal. Thus, the present book gives a good feedback to the increasing demands in developing effective precision linear quantum calculation methods for the study of linear and nonlinear optical properties of periodic and aperiodic polymeric structures with delocalized  $\pi$  system.

Goals and objectives of the study. Objective: to establish a relationship between the optical and magnetic properties, systematic scientific analysis of the nature of the interaction of metals with fullerenes, the study of nonlinear optical effects of porphyrins, fullerenes and carbon nanostructures.

To achieve these goals the following scientific and practical tasks should be performed:

- Optimization of geometrical structure: porphyrins, C<sub>60</sub> derivatives, exo- and endohedral metallofullerenes, fullerene-porphyrin dyads, polyacenes, carbon nanotubes;
- Conduct a comprehensive charge decomposition analysis of metal atoms with fullerene compounds;
- Explore the phenomenon of adsorption of metals on the surface of fullerenes;
- Investigate the linear and nonlinear optical effects of porphyrin derivatives, fullerenes, and carbon nanostructures;
- Assess the impact of the nature of substituents on the optical properties of fullerene hybrid materials;

- Determine the cause of the broadening of line in optical detection of magnetic resonance for the triplet excited states of porphyrins;
- Develop effective methods for the investigation of the electronic structure and nonlinear optical properties of polyatomic molecular systems.

*Object of research:* fullerenes, porphyrins, carbon nanostructures.

*Subject of research:* electronic structure, optical, and magnetic properties.

*Research methods:* ab initio methods, density functional theory methods, semiempirical methods, O (N) methods for linear calculations (QFMM, EM).

*Scientific novelty of the results:* The most significant new scientific results of the study are established the linear and nonlinear optical (NLO) properties of porphyrins derivatives and fullerene carbon nanostructures.

The radiative lifetime of phosphorescence lines and microwave signals in optical detection of magnetic resonance (ODMR) spectra are obtained using the B3LYP hybrid density functional and the quadratic response method. The zero-field splitting (ZFS) in the lowest triplet state,  $a^3B_{2u}$ , of FBP is calculated as an expectation value of spin–spin coupling operator using the self-consistent field wave function. The second-order contribution to ZFS from the spin–orbit coupling operator is found to be almost negligible. The interpretation of the ODMR spectrum is completed by computing the hyperfine tensors of the  $^{14}\text{N}$ ,  $^{13}\text{C}$ , and hydrogen atoms in the lowest triplet state. The most intensive phosphorescence emission corresponds to the  $T^z$ -spin sublevel of the  $a^3B_{2u}$  state, where the  $z$ -axis lies in the N–H direction of the FBP molecule in a qualitative agreement with ODMR data. The results indicate that the observed decay of the lowest triplet state of FBP molecule is determined by nonradiative deactivation. The calculated radiative rate constant for the  $T^z$  spin sublevel  $k_z = 2.65 \times 10^{-3} \text{ s}^{-1}$ .

The performed study of photoinduced isomerisation reaction of free base porphyrin molecule using the DFT-B3LYP method show that the reaction occurs in a stepwise pathway of isomerisation.

A novel  $\text{Pd}_2(\eta^2 - \text{C}_{60})$  structure with the two metal atoms bridging over a six-membered ring has been identified as the most stable arrangement of two palladium atoms on the surface of  $\text{C}_{60}$ . Both metal atoms benefit from  $\eta^2$  coordination at (6–6') junctions as well as some metal–metal interaction. Binding of Pd atoms to the fullerene is preferred over palladium dimerization.

Using a wide range of quantum-chemical methods the linear and nonlinear optical properties of [60]fullerene-chromophore dyads of different electron–donor character were analyzed in detail. It is demonstrated that in the case of investigated systems, traditional functionals poorly reproduce the values of first-order hyperpolarizability ( $\beta$ ) calculated using MP2 method. It turned out, however, that both Coulomb-attenuating model (CAM–B3LYP) and LC–BLYP functional give reliable electronic contributions to  $\beta$ . The analysis of the relations between the nature of the chromophore and the properties of the whole [60]fullerene-chromophore dyad shows that substitution of 2,1,3-benzothiadiazole by triphenylamine group lead to significantly larger values of first- and second-order hyperpolarizability.

The two-photon absorption cross section is also enhanced upon chromophore modification. For [60]fullerene-chromophore dyads the harmonic vibrational contributions to  $\beta$  have been observed to be much larger than the electronic counterpart. The calculations of vibrational contributions to  $\beta$  for fulleropyrrolidine reveal, however, very large anharmonicity effects.

The linear and nonlinear optical properties of C<sub>60</sub>-triphenylamine (TPhA) hybrids are reported. The synthesized materials were prepared following the 1,3-dipolar cycloaddition of azomethine ylides onto the skeleton of C<sub>60</sub> forming the TPhA-based monoadduct, equatorial bis-adduct and dumbbell C<sub>60</sub>. It was proved that in all considered cases, C<sub>60</sub> serves as an acceptor while triphenylamine unit acts as a donor. It was found that the total second-order hyperpolarizability of C<sub>60</sub>-TPhA-C<sub>60</sub> system is several times larger than that of TPhA-C<sub>60</sub>. The results of experimental measurements are supported by quantum-chemical calculations.

Electronic and vibrational nuclear relaxation (NR) contributions to the dipole (hyper)polarizabilities of the endohedral fullerene Li@C<sub>60</sub> and its monovalent cation [Li@C<sub>60</sub>]<sup>+</sup> have been carried out at the (U)B3LYP level. The obtained new results differ significantly from those reported previously using more approximate methods. The properties are compared with those of the corresponding hypothetical non-interacting systems with a valence electron transferred from Li to the cage. Whereas the NR contribution to the static linear polarizabilities is small in comparison with the corresponding electronic property, the opposite is true for the static hyperpolarizabilities. A relatively small, but non-negligible, NR contribution to the dc-Pockels effect is obtained in the infinite frequency approximation.

It is demonstrated that the functionalization of porphyrin by adding a metal atom significantly increases the NLO properties of the investigated systems. It was observed that increasing the size of the spacer chain from 0 to 8 carbon units almost linearly enhances the polarizability and second hyperpolarizability of [60]-H<sub>2</sub> P system.

A new approach has been developed for solving the eigenvalue problem for the oligomer chain systems based on localized molecular orbitals (LMO) of the separated fragments within the elongation method. The method performed in this work and implemented in elongation scheme yields excellent agreement with the conventional results. It has been demonstrated that the proposed algorithm for computing orbital energies and eigenvectors in elongation method reduces the CPU time usage up to 50 %.

Designed and implemented in software the new linear scaling technique for the study of compounds with delocalized electronic density.

*The practical significance of the results:* The research conducted in the dissertation is of great practical importance for the synthesis of optically active organic materials used in photonics to create a fundamentally new organic light-emitting diodes (LED) and to develop photoconductive and photosensitive elements for converting solar energy into electricity.

The developed linear scaling methods significantly reduce the CPU time of quantum studies for large multi-electron systems without significant loss of accuracy in total energy calculations compared to traditional methods of calculating the NLO.