First principles study of the structural, electronic and optical properties of crystalline o-phenanthroline

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In a comprehensive study, structural properties, electronic structure and optical response of crystalline o-phenanthroline were investigated. Our results show that in generalized gradient approximation (GGA) approximation, o-phenanthroline is a direct bandgap semiconductor of 2.60 eV. In the framework of many-body approach, by solving the Bethe–Salpeter equation (BSE), dielectric properties of crystalline o-phenanthroline were studied and compared with phenanthrene. Highly anisotropic components of the imaginary part of the macroscopic dielectric function in o-phenanthroline show four main excitonic features in the bandgap region. In comparison to phenanthrene, these excitons occur at lower energies. Due to smaller bond lengths originated from the polarity nature of bonds in presence of nitrogen atoms, denser packing, and therefore, a weaker screening effect, exciton binding energies in o-phenanthroline were found to be larger than those in phenanthrene. Our results showed that in comparison to the independent-particle picture, excitonic effects highly redistribute the oscillator strength.

Keywords: Organic compounds; o-phenanthroline; ab initio calculations; electronic structure; optical properties.

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1. Introduction

Due to many applications, such as organic light-emitting diodes, organic thin-film field-effect transistors, photovoltaic cells and sensors,1–3 a large number of physical and chemical studies have dealt with the organic compounds and their usages in the electronic and opto-electronic devices. Semiconducting organic materials including

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small $\pi$-conjugated molecules, i.e., molecular crystals, recently have attracted intense attention because of their amazing properties in many research areas of the electronic and opto-electronic physics as well as materials science.\textsuperscript{4–6} The actual potential practical applications, such as catalysis, electrical conductivity and superconductivity have made them promising compounds in electronic and photonic fields.\textsuperscript{7,8}

Excitonic states, i.e., the collective uncharged low energy electronic excitation involving the creation of bound electron–hole (e–h) pairs, are of the most interesting aspects of molecular crystals. In optical phenomena, due to the strong Coulomb attraction, a bound e–h is formed which can transport electronic excitation energies. In an accurate description of many optical properties, photoemission and photovoltaic effects, the excitonic couplings are essential to be into account. Developing the organic opto-electronic devices, such as organic light-emitting diodes and organic solar cells intensely depends on the excitonic effects. In other words, the use of organic semiconductors for electronic and opto-electronic applications is strongly dependent on the behavior of excitons.\textsuperscript{9,10} In the quest of effective solar cells, the organic ones have been proposed to reach a high level of electronic performance in low cost power conversion efficiency.\textsuperscript{11} However, the usage of materials in opto-electronic devices is in a direct relevant to the knowledge of optical properties. For example, in flat-heterojunction organic solar cells, the excitonic behavior in the optical responses determines the efficiency of device.\textsuperscript{12} Therefore, the use of these materials in solar cell devices is highly correlated to the knowledge of response functions in particular close to the energy bandgaps. In such a way, optical absorption spectra were theoretically calculated for a number of interesting organic systems including molecular crystals and biological molecules, such as anthracene and phenanthrene,\textsuperscript{13} tetracene,\textsuperscript{14} picene and pentacene\textsuperscript{15} and polymeric compounds, such as poly (para-phenylene),\textsuperscript{16} which are in an amazing accordance with the experimental reports. Recently, using \textit{ab initio}-based methods, the lowest ionization and excitation energies of various biologically important molecules have been calculated.\textsuperscript{17} These materials are $\pi$-conjugated systems, such as adenine, guanine, their isomers and other related planar heterocyclic. It has been found that the vertical excitation energies and the vertical ionization energies are mainly, but not exclusively, of $\pi-\pi^*$ and $\pi$ character, respectively.

1,10-phenanthroline (o-phenanthroline) with the molecular formula C\textsubscript{12}H\textsubscript{8}N\textsubscript{2}, similar to phenanthrene (C\textsubscript{14}H\textsubscript{10}), is an organic molecule in the zigzag geometry in which two carbon atoms are replaced by two nitrogen atoms with no conjunction to hydrogen atoms (Fig. 1). Phenanthrene is nonpolar while o-phenanthroline is a polar structure with a finite dipole moment originated from the presence of nitrogen as an electron acceptor.\textsuperscript{18} It is a well-known compound as a two-dentate ligand in coordination chemistry, forming the strong complexes with metal ions.\textsuperscript{19} Many organic–inorganic complexes including a metal mixed to o-phenanthroline as a ligand represent high interest in chemical researches. Due to the easy control of o-phenanthroline as ligand, in several interaction patterns, these complexes can