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Letter

# Calculation of ionization potential of amorphous organic thin-films using solvation model and DFT

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ABSTRACT

Density functional theory and polarizable continuum model are used to calculate ionization potential of thin-films of 12 organic molecules. Computed values are compared with experimental values obtained from ultraviolet photoemission spectroscopy. The excellent correlation shows that it is possible to determine the ionization potential of organic molecules in solid-state within ±0.15 eV of the experimental value. This method is useful for chemists in designing molecules for organic electronics.



## 1. Introduction

Organic electronics has attracted much attention in recent research activity in molecules and materials. Organics based light emitting devices (OLEDs), solar cells (OSC), and field effect transistors (FET) are important devices under development in electronic industry. In organic semiconductor devices, thin solid films of organic molecules are used as active or passive functional layers. Information about the charge (electron or hole) carrier levels in organic thin-films, and relative energy levels with respect to electrodes are needed in understanding and fabricating the devices. For example, in OLEDs multiple layers of organic thin-films are used [1]. Carrier injection and transport occurs in HOMO or LUMO levels of organic material. The difference in the energy levels at the interface of the layers determines the flow of carrier and formation of excitons (excited state of molecule). A method to calculate these energy levels of organic solids will be highly useful for a synthetic chemist in designing the structure of organic molecules for organic electronics.

Energy levels and properties of isolated organic molecules can be calculated theoretically. Energy levels and properties in solid thin-film are usually different from those of isolated molecule, due to interaction among the molecules in the solid-state. A method is required to modify the energy levels calculated theoretically for isolated molecules to obtain a value appropriate for solid films.

Ultraviolet photoemission spectroscopy (UPS) is one of the frequently used techniques to determine the vertical ionization potentials in solids [2]. This gives the HOMO level of solid films. The ionization potentials of organic solids determined by UPS were compared with experimental and computational values for isolated molecules [3–6]. Not

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surprisingly, there is a big offset between the values for molecules in gas phase and solid-state. There have been attempts to bridge this offset by appropriate theoretical models [7,8]. For example, Lee and Han used the crystal structure data and molecular cluster model in the DFT calculation, which is successful for a sufficiently a large cluster of CuPc ($n = 6$).

In this letter, a method is described to determine the ionization potential of large organic molecules in solid-state using DFT method and polarizable continuum model. The polarizable continuum model [9,10] has been very successful in calculating realistic values of energy properties of molecules in liquid-like condensed phase. We show that the computationally determined ionization potentials for twelve organic molecular solids agree well with the experimental values, validating the proposed method. A novel feature of our method is that no experimental data for the molecule, other than the molecular structure, is used.

## 2. Methods of computation

Twelve organic molecules, for which experimental values of ionization potential of solid films are known, were chosen for this study. Density functional theory (DFT) was used in all the calculations using Gaussian 03 [11]. The DFT method used here is based on the hybrid B3LYP functional [12]. The geometries of all the molecules were optimized at 6-31G (d) basis functions. Molecular cavity for polarizable continuum model (PCM), was built using united atom topological model [13], i.e. by putting a sphere around each atom except hydrogen. Hydrogen atoms are enclosed in the sphere of the atom to which they are bonded.

The molecule in solid was considered as solvated by the molecules of its own type. The solvent in the PCM calculation is defined by the dielectric constant, the number of solvent molecules in unit volume and radius of the molecule. Following methods were used to obtain these values. The dielectric constant, $\varepsilon$ was obtained by Clausius–Mossotti equation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\frac{\rho}{M}N_A\alpha$$

where $\rho$, $M$, $N_A$ and $\alpha$ are the density of material, molecular mass, Avogadro number and the electronic polarizability, respectively. $\rho N_A/M$ is reciprocal of the molecular volume. Molecular volume was obtained at 6-31G (d) level (tight option was taken in all the calculation for better accuracy). Isotropic polarizability (at zero frequency) of molecules was calculated for the optimized geometry of molecules at 6-31G (d) level. Radius of the molecule is defined as radius of a sphere which has equivalent volume of the concerned molecule.

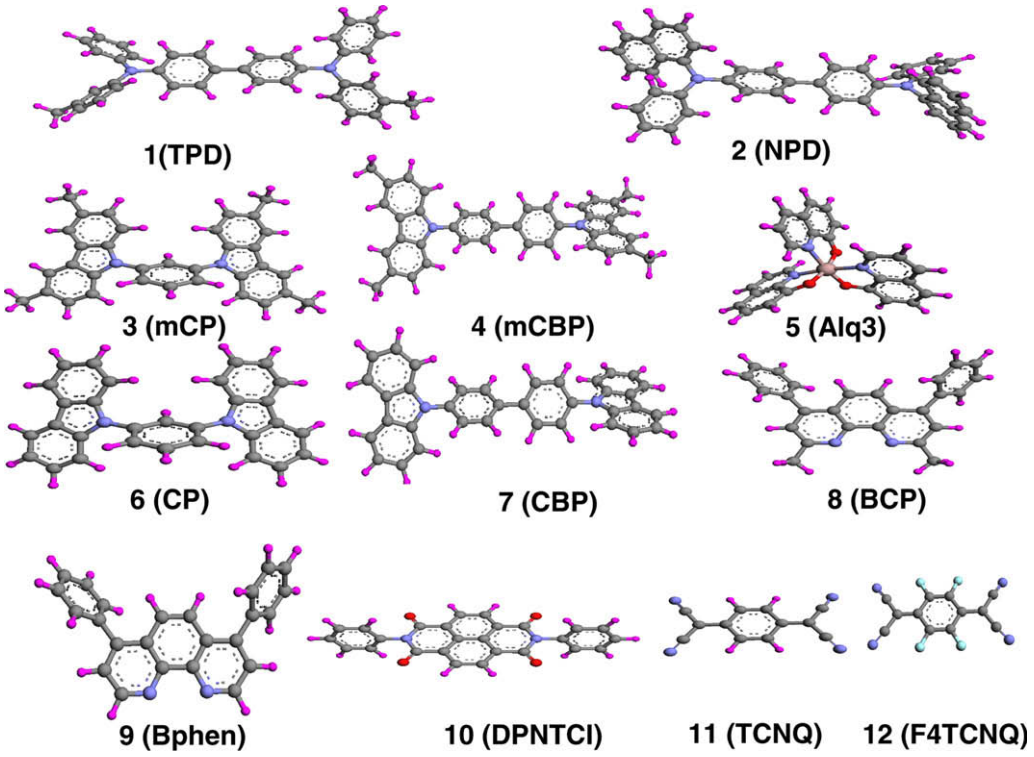


**Fig. 1.** Geometry optimized structure of molecules used in this study. 1: *N,N′*-bis(3-methylphenyl)-*N,N′*-diphenyl-[1,1′-biphenyl]-4,4′-diamine(TPD); 2: *N,N′*-bis-(1-naphthy)-*N,N′*- diphenyl-[1,1′-biphenyl]-4,4′-diamine (NPD); 3: *N,N′*-bis(3,6-dimethyl carbazolyl)-3,5-benzene (mCP); 4: 4,4′-*N,N′*-bis(3,6-dimetylcarbazolyl)biphenyl (mCBP); 5: Tris(8-hydroxyquinolate)aluminium(III) ($Alq_3$); 6: 4,4′-*N,N′*-bis-carbazolyl-biphenyl (CBP); 7: *N,N′*-dicarbazolyl-3,5-benzene (CP); 8: 4,7-diphenyl-1,10-phenanthroline (BCP); 9: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bphen); 10: *N-N′*-diphenyl-1,4,5,8-napthyl-tetracarboxyl-diimide (DPNTCI); 11: 7,7,8,8-tetracyano-p-quinodimethane (TCNQ); 12: 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-p-quinodimethane (F4TCNQ).