

Design, Synthesis and Computation of Functional Materials for Bio-analytical Applications

Introduction

The bottom-up approaches in nanoscience and nanotechnology have been achieved by several fundamental forces including electrostatic, charge transfer, dispersion, ion-mediated, hydrophobic, and π -stacking interactions of the extended aromatics, supported by directional H-bonding or amphiphilic interactions or by donor-acceptor interactions as electrostatic interaction of the negatively charged acceptor and the positively charged donor in charge-transfer complexes. Electron transfer (ET) occurs when electron density shifts from an atom of a molecule or molecule itself. The term ET referred to in electrochemistry is a mechanistic description of the thermodynamic concept of redox, wherein the oxidation states of both reaction partners change. In spectroscopy, electron is considered to undergo optical excitation from an occupied orbital to an empty allowed orbital. Both these ground and excited state orbitals may be identically delocalized over the molecule in those cases where there is no shift in electron density resulting in neither electron nor charge transfer. The condition for a charge transfer excitation in electronic spectroscopy dictates the ground and excited state orbitals to be distinctly delocalized over the molecule. In a charge transfer complex, a fraction of electronic charge is transferred between the molecular entities.

In an electron donor-acceptor / charge transfer complex, the attraction between molecules is created by a fraction of electronic charge transferred between the molecules, and the resulting electrostatic attraction provides a stabilizing force for the molecular complex. The nature of

attraction in an electron donor-acceptor complex is not a stable chemical bond and is much weaker than covalent forces; it is better characterized as a weak electron resonance. As a result, the excitation energy of this resonance occurs very frequently in the visible region of the electromagnetic spectrum. This produces the usual intense colors characteristic of these complexes. These optical absorption bands are referred to as charge-transfer bands or CT bands.

New nanoscale organic-inorganic composite materials have been developed including nanoparticles, nanolayers and nanorods for academic as well as industrial interest. The nature of engineered nanoscale organic-inorganic composite materials and their promising academic as well as industrial uses are noteworthy and are an on-going challenge within nanoscience and nanotechnology field. Density Functional Theory (DFT) based calculations and molecular dynamics simulations with molecular mechanics force fields revealed the nature of interparticle interaction, charge transfer and arrangement of molecular tectons in the nanocomposite structure and mechanism of formation.

The charge transfer (CT) assemblies of a donor (D) and an acceptor (A) aromatics are of great importance because of their inherent conducting properties. The charge transfer complexes from perylene with iodine or bromine showing low resistivity (8 ohm.cm) in comparison to their respective charge transfer inactive analogs. Charge transfer complex from a combination of well-known organic electron acceptor tetracyanoquinodimethane (TCNQ) and well-known organic electron donor tetrathiafulvalene (TTF) resulted in the discovery of first pure organic conductor. Separate parallel-aligned stacks of TTF and TCNQ molecules and charge transfer between them was the cause for increased conductivity. Therefore, fundamental to the success of the bottom-up approach is the ability to control electron transport across molecular and nanoscale components, exhibiting specific functions into electronic devices.

In view of the active components for nanoelectronic devices, development of CT nanostructures with long-range ordering of D and A components is mandatory. Hence, smarter supramolecular designs are required by which D and A molecules can be precisely positioned in a nanostructure with strong intermolecular interactions. Attempts to construct CT nanostructures were based on supramolecular host-guest design, wherein the pre-assembled networks of donor chromophores were mixed with the acceptor molecules. This strategy involved a simple molecular design as the donor assemblies were created by attaching well-known self-assembling motifs to the chromophores and the acceptor molecules got encapsulated into these assemblies via charge transfer interactions. Mixed donor-acceptor organization in a charge transfer complex can be alternate or face to face. Mixed stack CT organization of complementary donor and acceptor molecules provides long-range ordering of electrical dipoles leading to spontaneous electrical polarization in these materials, whose alignment direction could be switched by an external field.

Problem description

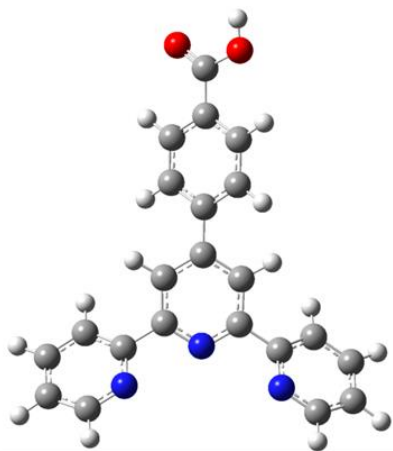
Covalent and non-covalent are the two major types of interactions that govern the formation of nanocomposites, complexes as well as molecular assembly. The covalent interaction arises spontaneously by specific surface treatment, whereas, the non-covalent interaction requires characteristic driving forces viz. ionic interaction (electrostatic interaction), van der Waals forces, dipole-dipole interaction (Keesom force), dipole induced interaction (Debye force) and dispersion interaction (London force) where, the strength of interaction lies between the two boundaries. The most important primary forces in the formation of nanocomposites have been covalent (60 - 80 kJ/mol), metallic as well as ionic (600 - 1200 kJ/mol) bond, while the

secondary forces (20 - 40 kJ/mol) included van der Waals forces and H-bonding (6-30 kJ/mol). Thus, there is demand for understanding the nature of interaction as well as frontier molecular orbitals involved for the formation of nanocomposites, complexes as well as molecular assembly.

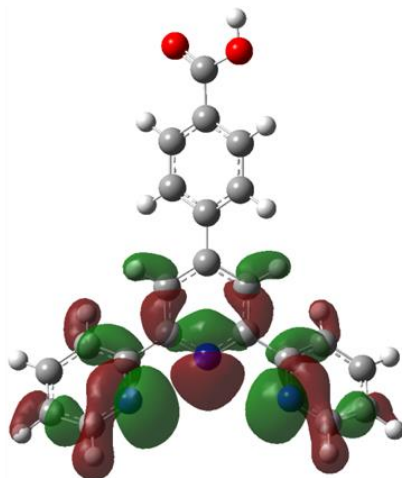
Proposed method

The density functional theory (DFT) calculations will be carried out using Gaussian 09 set of programs with the corresponding functional (B3LYP, Cam-B3LYP, M06, etc) and the corresponding basis set [3-21G, 6-31G (d,p), cc-pvdz, Lanl2DZ, SDD etc]. Molecular dynamics simulations will be performed using ADMP inbuilt in Gaussian 09 under the demand condition for the corresponding molecules / complexes / donor-acceptor moiety.

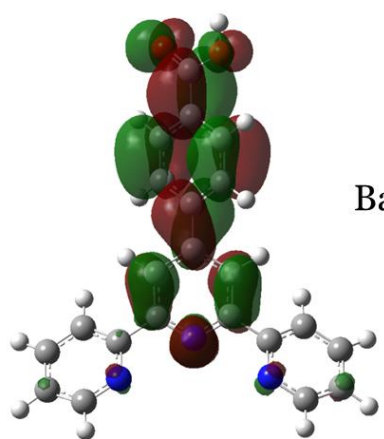
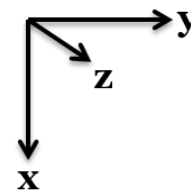
Here, some of the test results are for terpyridine ligand / graphene oxide / graphene oxide functionalized with terpyridine ligand ground state geometry as well as its frontier molecular orbitals.



DFT-B3LYP/6-31G
Energy = -1161.77 a.u.
Dipole moment = 2.08 Debye

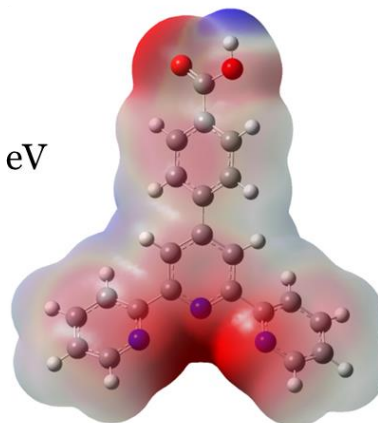


HOMO
Energy = 4.41 a.u.

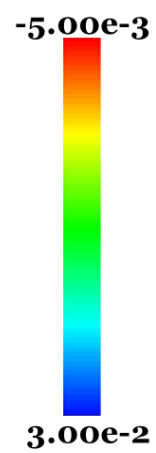


LUMO
Energy = -0.08 a.u.

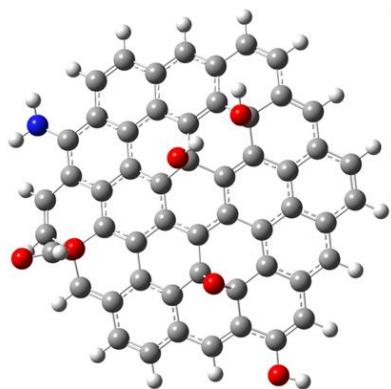
Band gap = 4.41 eV



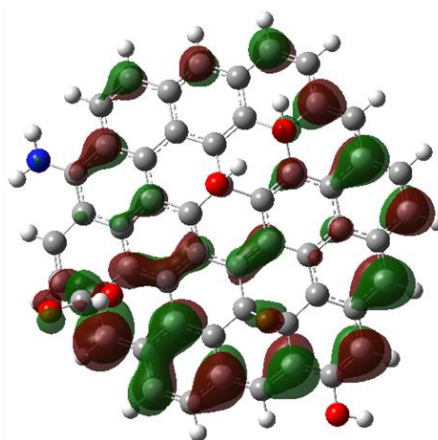
ESP Map



Graphene oxide:

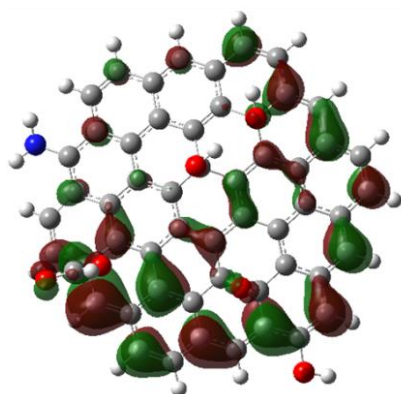


DFT-B₃LYP/6-31G
Energy = -2615.24 a. u.
Dipole moment = 3.53 Debye



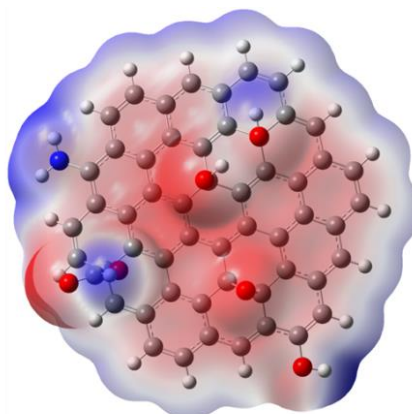
HOMO
Energy = -4.38 eV

Graphene oxide functionalized with terpyridine ligand:



LUMO
Energy = -2.91

Band Gap = 1.47 eV

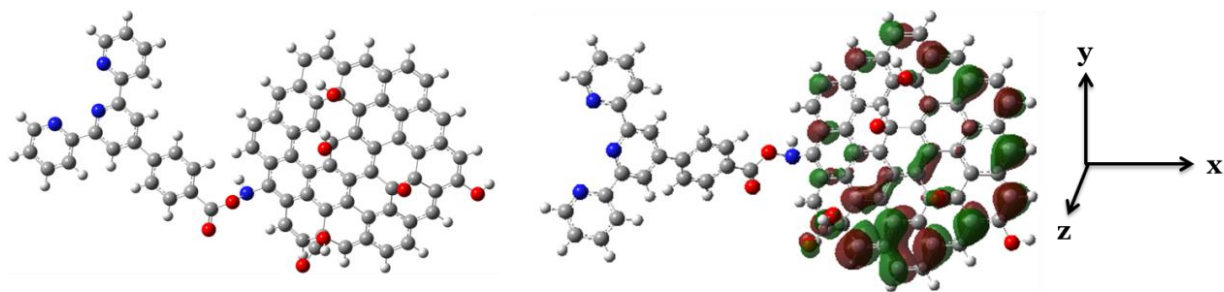


ESP

-5.00 e-3

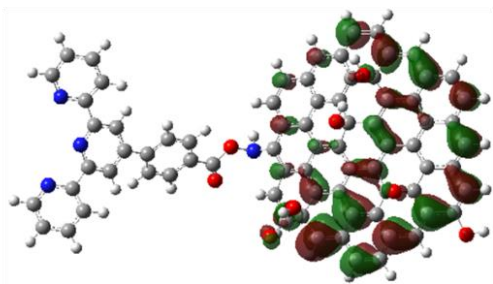


5.00 e-3



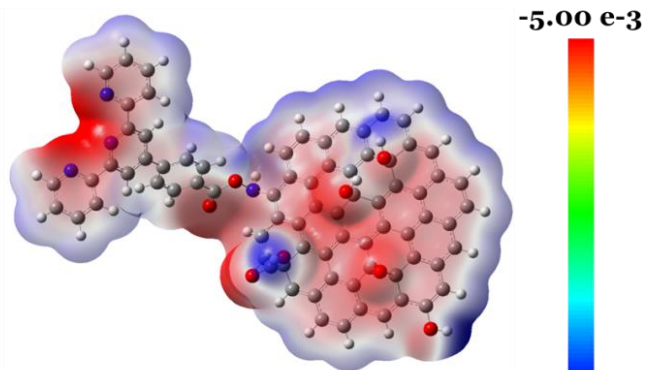
DFT-B3LYP/6-31G
Energy -3776.07a. u.
Dipole moment = 8.32 Debye

HOMO
Energy = -4.53 eV



LUMO
Energy = -3.04

Band Gap = 1.49 eV



ESP

5.00 e-3

Expected results:

This research will offer suitable frameworks to identify new and potential molecules and provide lead information for the development of donor-acceptor molecules / charge transfer complex / organic-inorganic composite. Moreover, computational chemistry based methodologies will allow us to derive guidelines at molecular level which can be used in a broader context to design new functional material. The outcome of the research is expected to have potentially high scientific impact on electronics and materials chemistry. These results will be summarized and published in a high impact peer-reviewed journal.