

Molecular Simulation of a Functional Polyimide Containing Electron-Donor and -Acceptor Groups on Gaussian 03 Program Package

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Background:

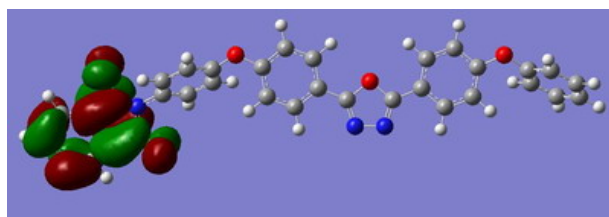
In recent years, silicon-based memory devices have increasingly faced the pressure to scale down cell sizes, important for research into the organic materials-based memory devices. In comparison to inorganic materials-based memory devices, molecular and polymeric memories exhibit low-cost potential, simplicity in structure, good scalability, potential for high-density data storage in 3-D arrays, and possibility of fabricating flexible devices.[1] Instead of information storage and retrieval by encoding “0” and “1” as the amount of charges stored in silicon-based devices, polymer memories store data in another form, for instance, based on the high- and low-conductivity response to an applied voltage.

In our work, a functional polyimide (P(BPPO)-PI) containing both electron donor (oxadiazole) and acceptor (phthalimide) moieties was designed and synthesised. Under the excitation of an electric field, charge transfer occurs between the donor and acceptor moieties, triggering the electrical conductance transition from the low-conductivity (OFF) state to the high-conductivity (ON) state. To understand the mechanism underlying the electrical transition, electronic properties of the polyimide, including molecular orbitals, dipole moments, and electrostatic potential (ESP) surfaces, were studied with the Gaussian 03 program package.

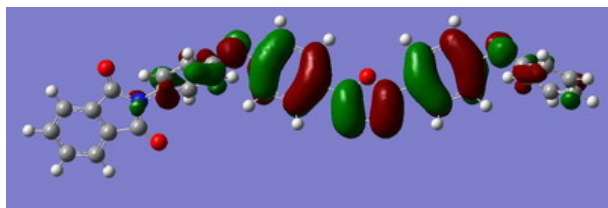
Molecular Simulation:

Molecular simulation for the P(BPPO)-PI molecule at the ground state was carried out with the density function theory (DFT), using the Becke’s three-parameter

functional with the Lee, Yang and Parr correlation functional method (B3LYP) and the basis set 6-31G with d function added to heavy atoms (in short, DFT B3LYP/6-31G(d)).[2] The calculated molecular orbitals of the polyimide are shown in Figure 1. The highest occupied molecular orbital (HOMO) is located mainly on the oxadiazole moiety, while the lowest unoccupied molecular orbital (LUMO) is located on the phthalimide moiety, indicating that in the copolymer, the oxadiazole moiety acts as the electron donor and the phthalimide moiety acts as the electron acceptor. Under an electric field, electrons will transfer from the donor moiety to the acceptor moiety, forming a charge transfer state. The generated holes at the HOMO can delocalise to the conjugated oxadiazole moieties, giving rise to an open channel for the charge carriers (holes) to migrate through. As a result, the POXD-PI device switches from the initial low-conductivity state to the high-conductivity state.



LUMO



HOMO

Figure 1. Molecular orbitals of the functional polyimide

To illuminate the above charge transfer process, the electronic properties of the P(BPPO)-PI molecule at the excited state were studied with configuration interaction involving single electron excitations (CIS) method and the same basis set as the calculation for the ground state.[3] As shown by the ESP surfaces in Figure 2, in comparison to P(BPPO)-PI at the ground state, P(BPPO)-PI at the excited state

exhibits larger negative ESP regions around the O atoms in the phthalimide group, indicating that under excitation, the electron will transfer to the phthalimide moiety from other moieties in the molecule. This electronic process is consistent with the electric field induced electron transfer process from the oxadiazole moiety to the phthalimide moiety, as mentioned above. The electron transfer process is also supported by the enhanced dipole moment of P(BPPO)-PI at the excited state (3.06 Debye) in comparison to that at the ground state (2.82 Debye).

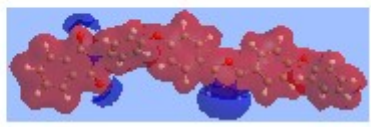
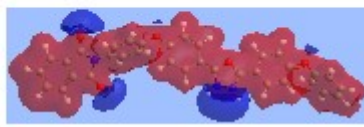
Properties	Ground State	Excited State
Dipole Moment	2.82 Debye	3.06 Debye
ESP Surface		

Figure 2. Dipole moments and electrostatic potential (ESP) surfaces for the ground and excited states. For the ESP surfaces, the positive ESP regions are in red, while the negative ESP regions are in blue.

Computing Resources

The Gaussian 03 CIS calculation is I/O intensive and can create very huge scratch files during the job execution. In our case, the rwf file created can be as large as 800GB. Hence, the disk access speed and disk capacity is crucial for the success of the calculation jobs. At HPC, the 2TB GPFS files system is a parallel file system and has faster access speed. It serves out purpose very well.

References:

- [1] Stikeman, A. *Technol. Rev.* **2002**, *105*, 31-31.
- [2] Frisch, M. J. *et al.*, *Gaussian 03 (Revision E. 01)*, Gaussian, Inc.: Wallingford, CT, 2008.
- [3] Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135-149.