Report to BASF for the period Sept. 2006-August 2007

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Over the past year, we focused our work on two aspects in the BASF project. The first one deals with *ab initio* calculations of charge transfer integrals and band structures of organic molecular crystals of interest as charge transport materials. The second deals with a statistical analysis of charge transfer and site energy data for amorphous Alq3 samples in relation to charge carrier mobility approximations based on the effective medium approach (EMA).

- **Ab initio calculations of transfer integrals and band structures of crystalline systems.**

1. *Theoretical study of charge transfer integrals of phenanthroline-based molecular systems.*

In these compounds, the dimer HOMO/HOMO-1 or LUMO/LUMO+1 energies are very close, so that the usual approximation of a "pure state model" fails in this situation. A new definition of "effective transfer integrals" based on "mixed states" was proposed. This work was recently published in the Journal of Chemical Physics (H. Li, J.L. Bredas, and C. Lennartz, J. Chem. Phys. 126, 164704 (2007)).

2. *Band structure calculations on phenanthroline-based molecular crystalline structures and on a quasi 1-D BCP chain model*.

The band structure calculations show that the dispersions of both the conduction band (CB, for electron transport) and the valence band (VB, for hole transport) are in very good agreement with the "effective transfer integrals" for both electron and hole transfers obtained in the manuscript referred to above. This work is now completed and a joint Georgia Tech-BASF manuscript is in preparation.

3. *Preliminary results of a study on site-energy differences*.

Taking a Bphen dimer with the geometry obtained from the crystal structure, we have studied the change in dimer site energy difference when a dimer is embedded in a simulated crystal structure, with different radius cut-offs. For all the surrounding atomic sites in the simulated crystal structure, point charges obtained from "Mulliken populations" are used. The numbers of molecules considered in the "outer shell" which simulates the crystal environment amount to 20, 28, and 96. The results are given in the table below, with D1 being the bare dimer, and D2 to D4 being the dimers with the various point-charge backgrounds indicated above. No convergence on the site energy difference is reached. The results show that the "point-charge-background" approximation appears to be too simplified and a more careful study should be carried out. Such studies will be carried out in the next phase of the project.

	ε_{1A}	ε_{2A}	$\Delta\varepsilon$
D1	-2.901	-3.076	0.175
D2	-2.813	-3.063	0.250
D3	-2.826	-3.112	0.286
D4	-2.826	-3.090	0.264

- **Statistical analysis and the EMA mobility approximation for amorphous Alq3 systems.**

1. *Transfer integral and site energy calculations on amorphous Alq3 systems*.

Two sample morphologies of amorphous Alq3 were provided by Professor Wolfgang Wenzel. In the first sample (781 pairs), periodic boundary conditions were not considered; they were in the second sample (1428 pairs), along the X and Y directions. Transfer integral and site energy results on both samples were provided to Prof. Jenny Nelson's group at Imperial College. The Monte Carlo simulations are completed and a manuscript is in preparation, the first draft being written by the group at Imperial College.

The electron and hole mobilities obtained from the MC simulations are given in the figure below (provided by Joe Kwiatkowski from Imperial College).

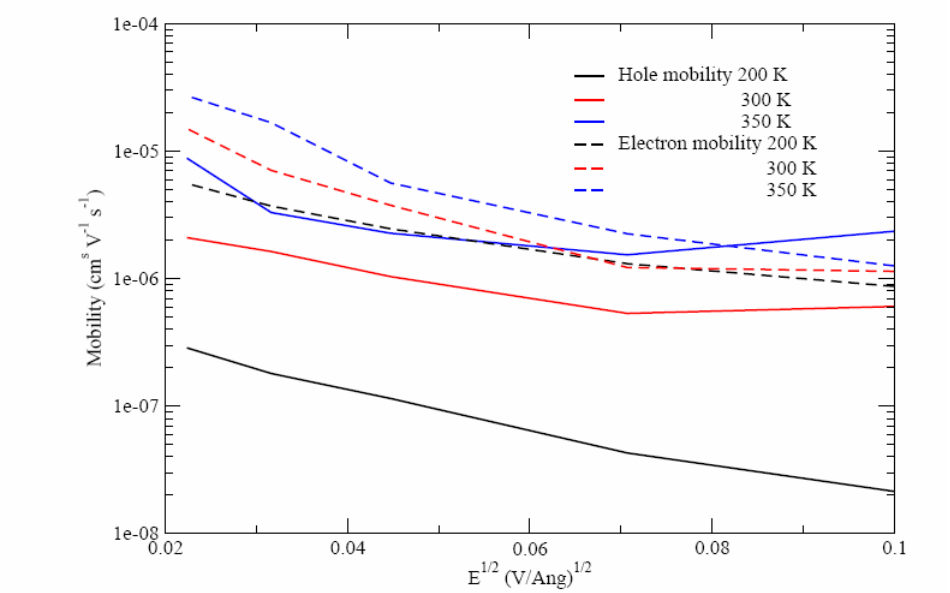
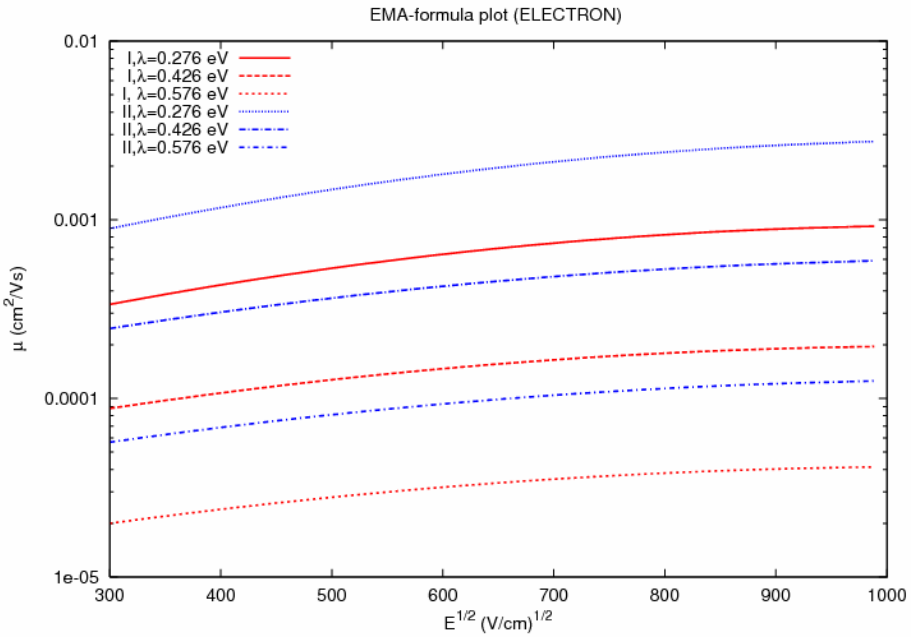
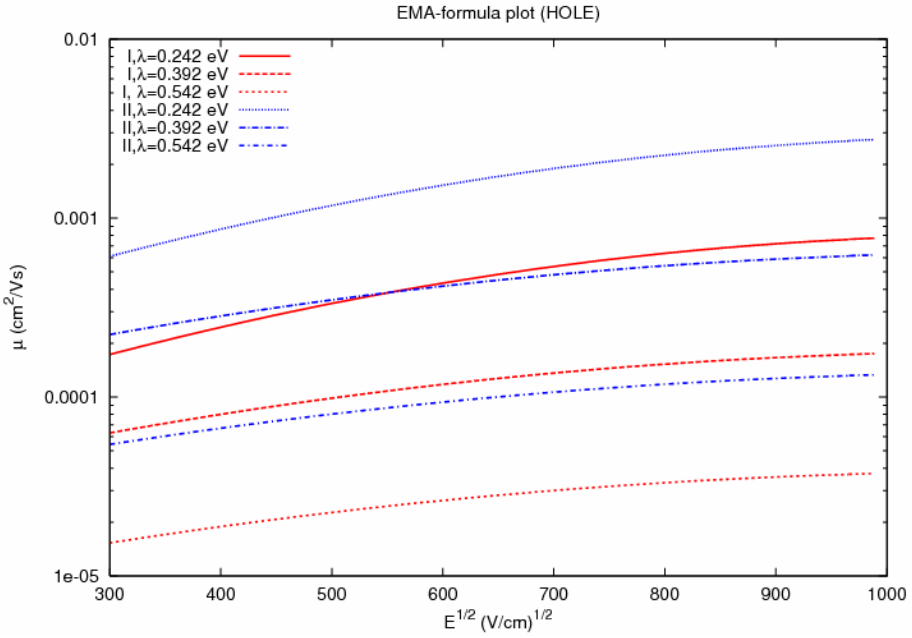


Figure 10: *Hole vs. electron mobilities. R030706 with lateral PBC turned on, single unit cell.*

2. *Statistical analysis of transfer integral and site energy data for amorphous Alq3.*

We also estimated the effective drift mobilities of electron and hole in the amorphous system on the basis of the analytical study of I. I. Fishchuk and H. Bässler, using the effective medium approach (EMA). The electron and hole mobilities obtained with the EMA formula are shown in the two figures below. The mobilities estimated from the two samples are in good agreement with each other. For electron mobility, the EMA approximation provides a value which is about one order of magnitude larger than the experimental result (1.2×10^{-6} cm^2/Vs for an electric field of 5.5×10^5 V/cm). The hole mobility obtained from the EMA approximation is of the same order of magnitude as the electron mobility; however, it is rather difficult to compare to experiment as the mobility measurements differ quite widely and range from 10^{-5} to10^{-9} cm^2/Vs.


EMA-formula plot (ELECTRON)
I,λ=0.276 eV
I,λ=0.426 eV
I, λ=0.576 eV
II,λ=0.276 eV
II,λ=0.426 eV
II,λ=0.576 eV
0.01
0.001
0.0001
1e-05
μ (cm²/Vs)
300
400
500
600
700
800
900
1000
E^1/2 (V/cm)^1/2


EMA-formula plot (HOLE)
I,λ=0.242 eV
I,λ=0.392 eV
I, λ=0.542 eV
II,λ=0.242 eV
II,λ=0.392 eV
II,λ=0.542 eV
0.01
0.001
0.0001
1e-05
μ (cm²/Vs)
300
400
500
600
700
800
900
1000
E^1/2 (V/cm)^1/2