Theoretical study of the charge transport properties within a smectic layer of dioctylterthiophene molecules

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Abstract

Molecular organic semiconductors currently stimulate a huge interest in view of their applications as active materials in a new generation of opto-electronic devices. Intermolecular charge transport in organic layers is a key process in all devices. The molecular parameters entering into the Marcus rate of the charge transfer between two interacting molecules can be estimated with the help of quantum-chemical calculations [1]. The Marcus expression features two main parameters: the reorganization energy λ and the transfer integrals t. Unlike λ, the t parameter that characterizes the amplitude of the interactions between adjacent molecules is strongly affected by the supramolecular order.

We describe here at the theoretical level charge transport properties within a smectic layer of dioctylterthiophene molecules deposited on a silanized glass substrate. Smectic phases have the advantage to prevent the formation of grain boundaries that hamper 2D charge transport.

Methodology

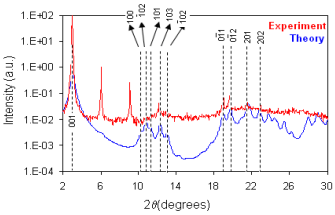
❑ Building of the system – Two molecules in the primitive cells
❑ Validation of the COMPASS force field - Comparison between theoretical and experimental XRD spectra
❑ Optimization (COMPASS force field)
Cell composed of 64 molecules (Periodic Boundary Conditions)
Starting point for the MM/MD simulations

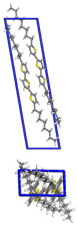
❑ On the optimized structure

Molecular dynamics
1°) NVT, 100ps, 340K (to reach the equilibrium state)
2°) NVT, 90ps, 340K (to analyze the trajectory)

❑ For each frame (every 30fs) of the second dynamics on the optimized structure
Calculation of the centre of mass of all molecule.
Estimation of the electronic splittings for all pairs of molecules by the Hartree-Fock semi-empirical INDO (Intermediate Neglect of Differential Overlap) method.

XRD spectra





a (Å)	8.78
b (Å)	4.75
c (Å)	29.50
α (°)	89.30
β (°)	102.00
γ (°)	93.00

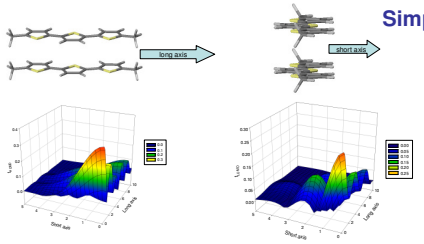
The unit cell that best reproduces the experimental X-ray diffraction spectrum is composed of two molecules, with a vertical translation of one molecule with respect to the other by about a thiophene unit (2.5 Å).

Marcus theory

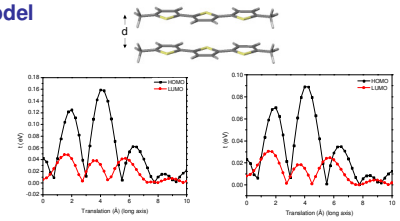
$$k_{hop} = \frac{2\pi}{\hbar} t^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{\lambda}{4k_B T}\right]$$

K_{hop}: Rate of charge hopping
t : Electronic coupling (transfer integral) between neighboring molecules
λ: Reorganization energy for the intermolecular transfer
h : Planck's constant
K_B : Boltzmann constant
T : Temperature

Simple model



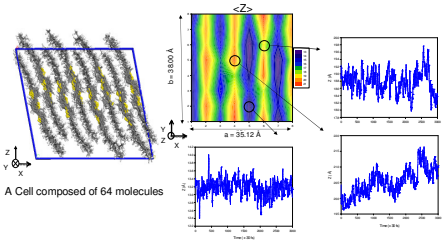
The variation of the t values is more pronounced for the displacement along the short axis.
In general, t_{HOMO} is larger than t_{LUMO}. However, for certain configurations t_{LUMO} can exceed t_{HOMO}.



Same trends for the variation of t as a function of a translation along the long axis for two different distances d.
The magnitude of t is reduced when increasing d between the molecules. This is due to the smaller overlap with increasing d.

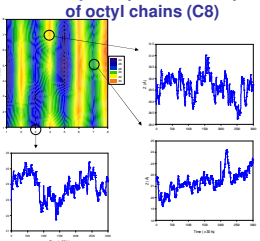
Molecular dynamics

The smectic layer

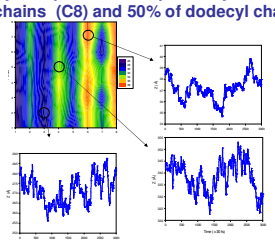


A Cell composed of 64 molecules

The smectic layer deposited on top of a layer of octyl chains (C8)



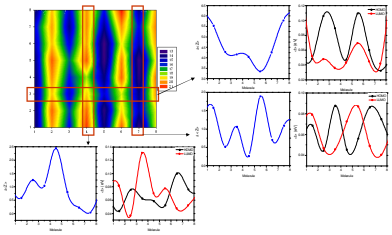
The smectic layer deposited on top of a layer composed of 50% of octyl chains (C8) and 50% of dodecyl chains (C12)



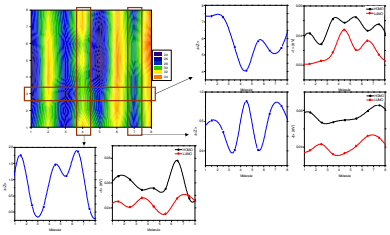
There is no molecular interpenetration between neighboring layers. The system is well ordered. The variation of <Z> does not exceed 2 Å in the bulk, 3 Å when the smectic layer is deposited on top of a layer of octyl chains (C8) and 5 Å when it is deposited on a layer composed of 50% of octyl chains (C8) and 50% of dodecyl chains (C12).

Charge transport properties

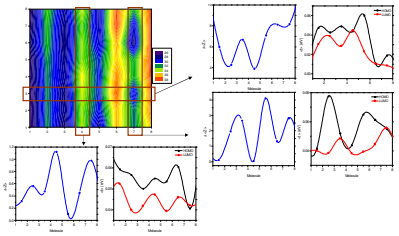
The smectic layer



The smectic layer deposited on top of a layer of octyl chains (C8)



The smectic layer deposited on top of a layer composed of 50% of octyl chains (C8) and 50% of dodecyl chains (C12)



-In general, the HOMO transfer integrals are larger than the LUMO values.
-The magnitude of the transfer integrals does not change significantly when dodecyl chains are introduced.

Conclusions

- The charge transport properties are highly sensitive to the supramolecular disorder.
- The HOMO transfer integrals are larger than the LUMO values, which implies that the system should exhibit a larger mobility for holes.
- The disorder induced by the roughness of the silanized substrate does not have a strong influence on the charge transport properties.

[1] Brédas, J.L.; Beljonne, D.; Coropceanu, V.; Cornil, J.; Chem. Rev. 2004, 104, 4971

Acknowledgment: ***This work has been supported by the Région Wallonne project ETIQUEL and by the Belgian National Fund for Scientific Research (FNRS).***