

Charge mobility of discotic mesophases: a multiscale quantum/classical study

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LEA meeting

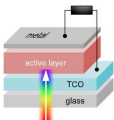
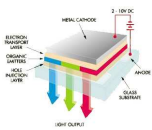
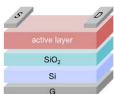
*Fundamental and Applied Macromolecular Science:
Toward Next Generation Materials*

29-31 January 2007, Strasbourg, France

The pdf file of this presentation is available here

<http://www.mpip-mainz.mpg.de/~andrienk/>

Function-adjusted material properties



- **Field-effect transistors**

- high electron/hole mobilities (ordered morphology)

- **Light-emitting diodes**

- high charge mobilities
- efficient photon absorption
- large recombination area (disordered morphology)

- **Solar cells**

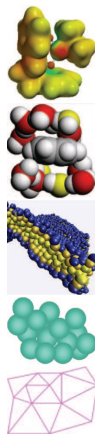
- high electron/hole mobilities
- small recombination
- efficient percolation of charges (ordered morphology)

Structure → Morphology → Properties

How can theory/simulations be useful?

- **Morphology:** coarse-grained MD, MC, SCF
- **Self-organization:** MC, MD, SCF
- **Charge transport:** Markus-Hush formalism, Green functions, KMC, DFT
- **Excited states:** TDDFT, CI

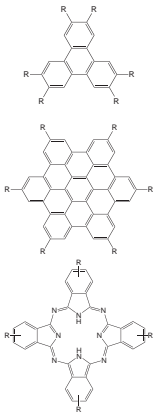
Can we predict material properties prior to synthesis of compounds?



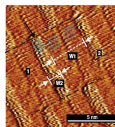
Triphenylenes, hexabenzocoronenes, phthalocyanines ...

Properties

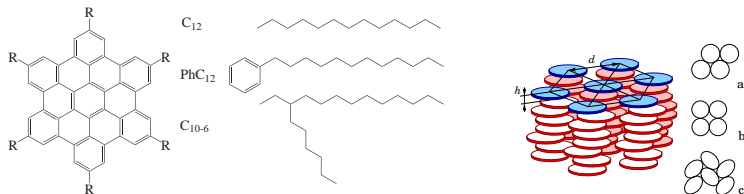
- Easy to process
- Self-organize into columnar structures
- One-dimensional transport of charges along columns ($\mu \sim 0.5 \text{ cm}^2/\text{V sec}$)
- Self-healing upon heating
- Actively studied for use in solar cells and OFETs



- A. M. van de Graats et al, **Advanced Materials** 1999
 L. Schmidt-Mende et al, **Science** 2001
 H. J. Räder et. al. **Nat. Mat.** 2006
 M. Van der Auweraer, F. C. De Schryver **Nat. Mat.** 2006



Derivatives of hexabenzocoronenes



Experimental data

| | S | d, nm | h, nm |
|-------|------|-------|-------|
| C12 | 0.84 | 2.86 | 0.35 |
| C14 | - | 2.66 | 0.367 |
| C16 | - | 2.66 | 0.372 |
| PhC12 | 0.95 | 3.4 | 0.35 |

- I. Fischbach et al **J. Phys. Chem. B** (2002)
 A. Fechtenkötter et al **Angew. Chem.** (1999)
 S. P. Brown, I. Schnell et al **J. Am. Chem. Soc.** (1999)
 P. Herwig et al **Adv. Mater.** (1996)

Development of the force-field

Quantum chemistry calculations. Matching calorimetric, X-ray scattering, and NMR data.

Potential energy

$$U = \sum_{\text{bonds}} \frac{1}{2} K_b (r - r_0)^2 +$$

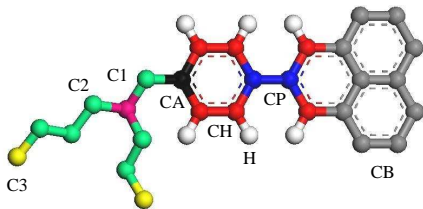
$$\sum_{\text{angles}} \frac{1}{2} K_\theta (\theta - \theta_0)^2 +$$

$$\sum_{\text{dihedrals}} \sum_{n=1}^3 \left[\frac{V_n}{2} + (1 + (-1)^{n+1} \cos n\phi) \right] +$$

$$\sum_{\text{impropers}} K_d (\psi - \psi_0)^2 +$$

$$\sum_i \sum_{j>i} \left[\frac{1}{4\pi\epsilon\epsilon_0} \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} \right]$$

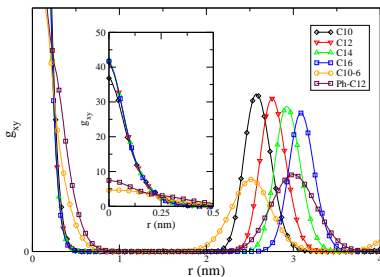
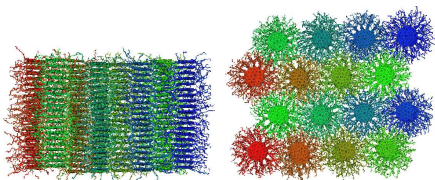
Atom types



A. von Lilienfeld and D. Andrienko *J. Chem. Phys.* (2005)

D. Andrienko et al *J. Chem. Phys.* (2006)

MD simulations of HBC derivatives



| system | S | d, nm | h, nm |
|--------|-------------|-------------|--------------|
| C10 | 0.98 | 2.57 | 0.367 |
| C12 | 0.84 | 2.86 | 0.35 |
| | 0.98 | 2.76 | 0.366 |
| C14 | - | 2.66 | 0.367 |
| | 0.98 | 2.93 | 0.367 |
| C16 | - | 2.66 | 0.372 |
| | 0.98 | 3.09 | 0.368 |
| C10-6 | 0.85 | 2.54 | 0.363 |
| PhC12 | 0.95 | 3.4 | 0.35 |
| | 0.93 | 3.00 | 0.379 |

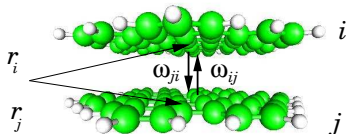
D Andrienko, V Marcon, K Kremer

J Chem Phys (2006)

Master equation approach

Master equation

$$\frac{\partial P_i}{\partial t} = \sum_j [\omega_{ij} P_j (1 - P_i) - \omega_{ji} P_i (1 - P_j)]$$



P_i - probability of a charge to be on a site i

ω_{ij} - hopping rate from site j to site i

Mobility

$$\mathbf{v} = \sum_{ij} \omega_{ji} P_i (1 - P_j) (\mathbf{r}_j - \mathbf{r}_i)$$

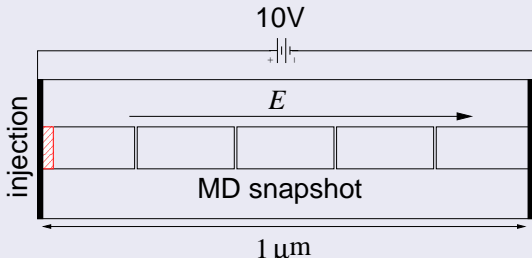
$$\mathbf{v} = \mu \mathbf{E}$$

Yu et al *Phys. Rev. Lett.* (2000)

B. Derrida *J. Stat. Phys.* (1983)

KMC simulations of time-of-flight experiments

TOF KMC simulation geometry



- inject a charge
- pick a neighboring site j at random, weighting by its rate ω_{ij}
- advance waiting time by $t_i = \frac{-\log \xi}{\sum_{j=0}^N \omega_{ij}}$, where ξ is a random number.

Marcus rates

Marcus expression for charge transfer rates

$$\omega_{ij} = \frac{|J|^2}{\hbar} \sqrt{\frac{\pi}{\lambda kT}} \exp \left[-\frac{(\Delta G - \lambda)^2}{4\lambda kT} \right]$$

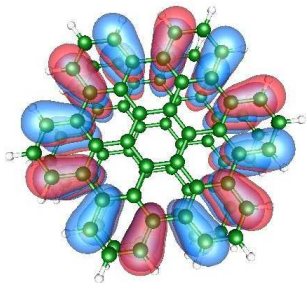
$|J|$ - transfer integral

$\Delta G = \mathbf{E} \cdot \mathbf{r}$ - free energy difference
between initial and final states

λ - reorganization energy

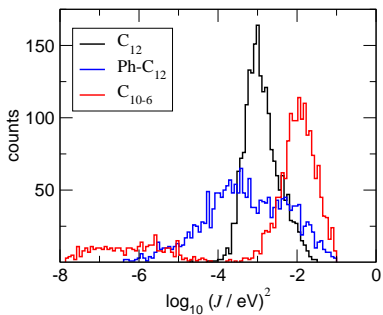
Kirkpatrick et al **in preparation** (2006)

K. F. Freed and J. Jortner **J. Chem Phys.** (1970)

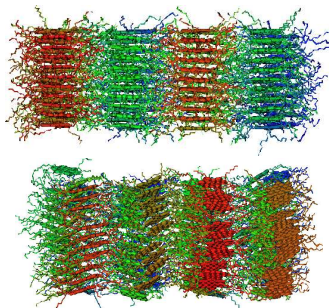


Geometry optimization UB3LYP,
6-31g** basis set. HOMO
splitting or a monomer electron
density - ZINDOS

Histograms of the transport integral

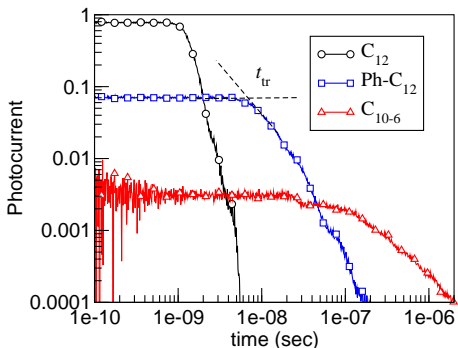


Histograms of $\log_{10}(J^2/eV^2)$



MD snapshots of C_{12} and C_{10-6} derivatives.

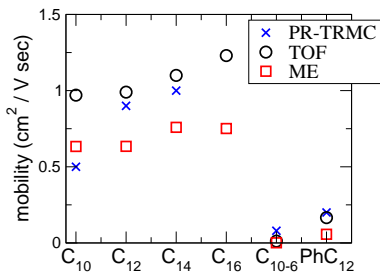
Time of Flight simulations



Photocurrent transients (holes only)

- $U = 10$ Volt
- $d = 1 \mu\text{m}$
- average over 200 MD snapshots
- average over 1000 transients per snapshot

KMC, ME, and experimental (PR-TRMC) mobilities



Electron (e) and hole (h) mobilities.

| compound | μ_{exp} | μ_{ToF}^e | μ_{ToF}^h | μ_{ME}^e | μ_{ME}^h |
|-------------------|--------------------|----------------------|----------------------|---------------------|---------------------|
| C ₁₀ | 0.5 | 0.22 | 0.75 | 0.14 | 0.49 |
| C ₁₂ | 0.9 | 0.23 | 0.76 | 0.14 | 0.49 |
| C ₁₄ | 1 | 0.27 | 0.80 | 0.17 | 0.59 |
| C ₁₆ | - | 0.29 | 0.91 | 0.17 | 0.58 |
| C ₁₀₋₆ | 0.08 | - | 0.01 | 6e-4 | 0.003 |
| PhC ₁₂ | 0.2 | 0.036 | 0.13 | 0.012 | 0.045 |

J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, D. Andrienko [cond-mat/0701382](https://arxiv.org/abs/cond-mat/0701382)

Conclusions

- Molecular disorder decreases charge mobility
- Presence of [static] defects kills 1D charge transport
- Temperature dependence of the mobility agrees well with the experiments

Message to take home

It is possible to predict not only trends, but also values of mobilities. This can be done without fitting parameters, starting only from molecular structures.

Collaborations and financial support

Collaborators

- Valentina Marcon, Thorsten Vehoff, Kurt Kremer (MPIP Mainz)
- James Kirkpatrick and Jenny Nelson (Imperial College London)
- Anatole von Lilienfeld-Toal and Mark Tuckerman (New York University)
- Numerous discussions with the members the group of Prof. Müllen.

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