Simulation of charge transport in organic materials

Denis Andrienko

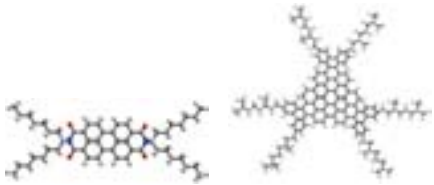
Max Planck Institute for Polymer Research

Japan-Germany joint workshop
Kyoto, 21-23 January 2009

Max Planck Institute for Polymer Research

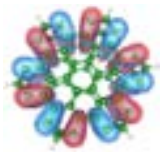
Location: Mainz, Germany. Founded 1983, 450-500 employees [ca 300 reseachers]. Annual budget 24 Mio Euro, 330 papers/year. 6 departments (synth. chemistry, functional materials, theory and simulations, NMR, biomaterials, surfaces and interfaces)

Organic Electronics Group



Valentina Marcon

rational compound dsesign
atomistic simulations of discotics:
HBC, perylene, trizigzag

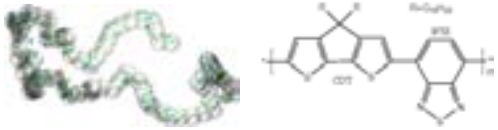


Alexander Lukyanov

systematic coarse-graining
force-matching
Alq3, donor-acceptor polymers

Thorsten Vehoff

conducting polymers
organic crystals
atomistic force-fields



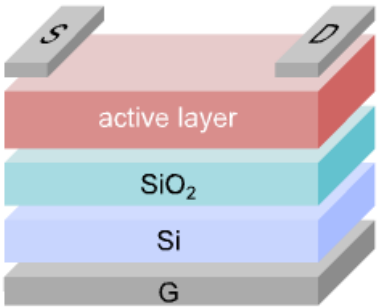
Victor Rühle

coarse-graining
large time- and length- scale simulations
conjugated polymers

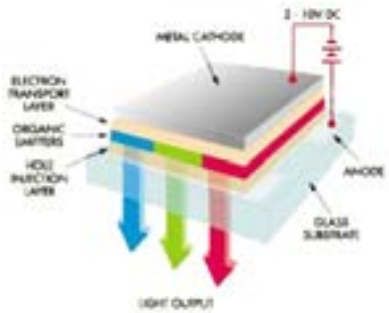
www.mpip-mainz.mpg.de/∼andrienk/

Aims

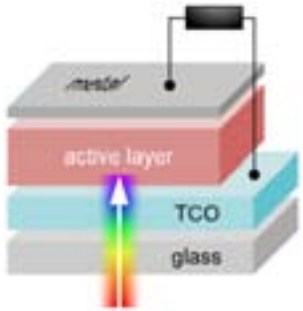
To replace active **inorganic** layers in FETs, LEDs and solar cells with suitable **organic** films (OFETs, OLEDs, etc).



Field-effect transistors



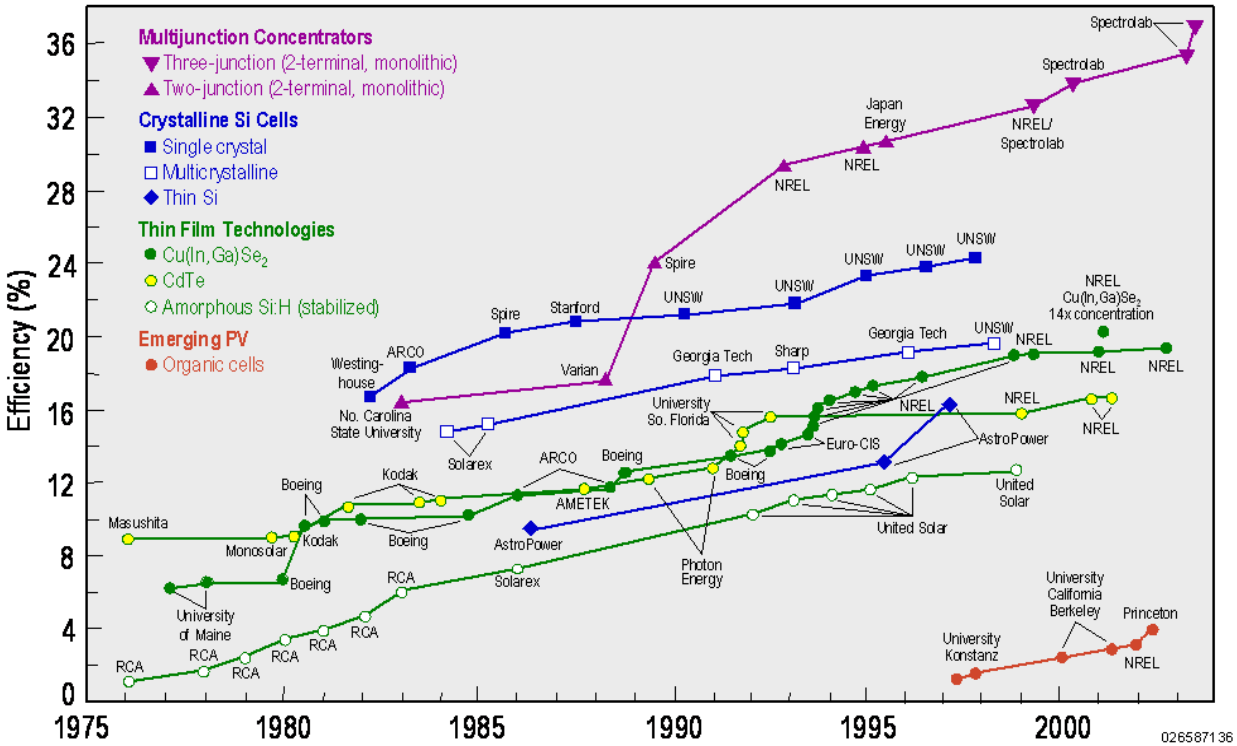
Light-emitting diodes



Solar cells

Requirements: high charge carrier mobilities (conjugated polymers, discotic LCs), controlled morphology (self-organizing materials).

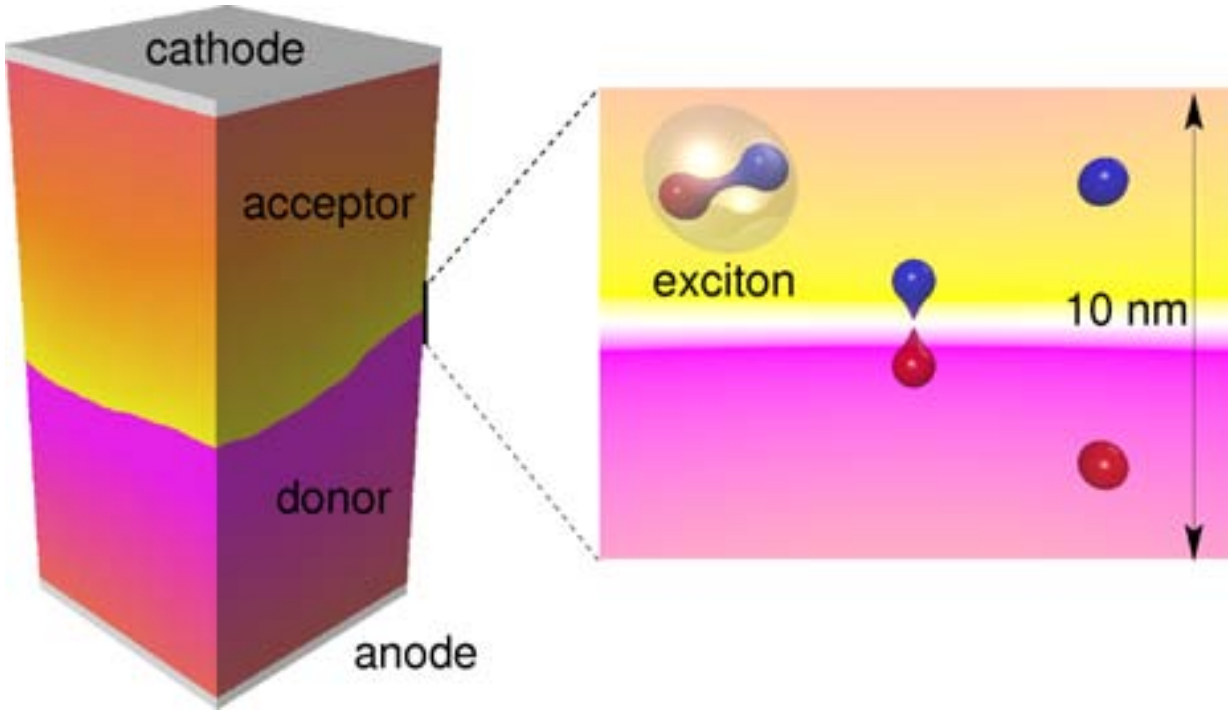
Energy conversion efficiency



12% efficency solar cell having $1\mathrm{m}^2$ in a full sunlight at noon at the equator will produce 120 watts of peak power.

Primary task: improvement of **efficiencies** and **life-times**.

Solar Cell Prototype

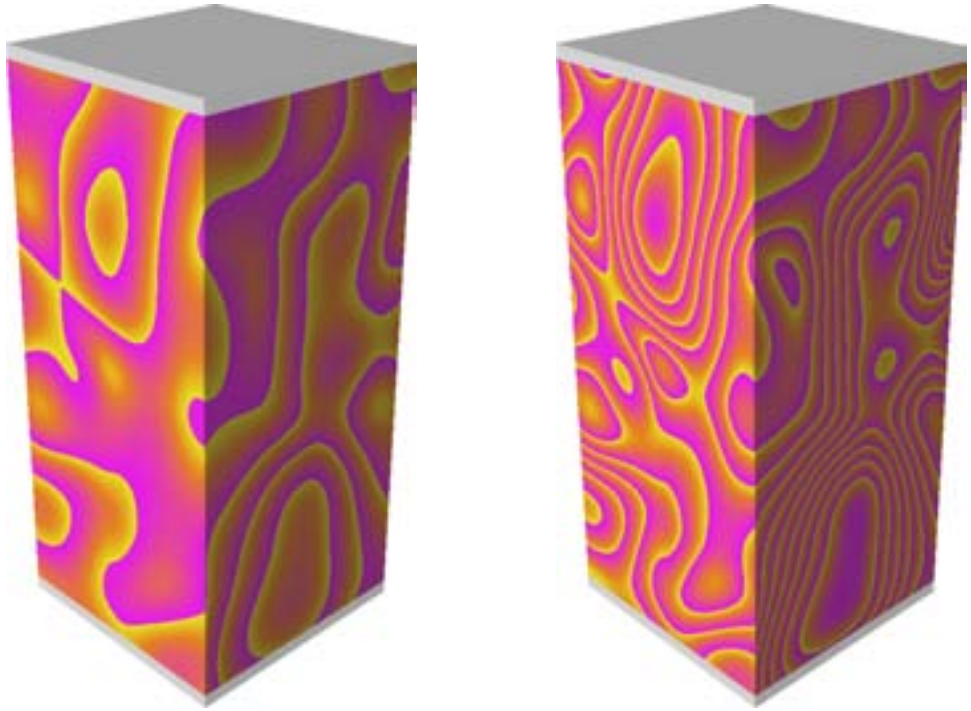


(1) photon absorption (2) exciton dissociation (3) charge transport

Only the excitons generated within 10 nm of the interface have a chance to dissociate, most excitons decay prior to dissociation.

C. W. Tang, **Appl. Phys. Lett.** 48, 183 (1986) ; G. A. Buxton and N. Clarke **Phys Rev B** (2006)

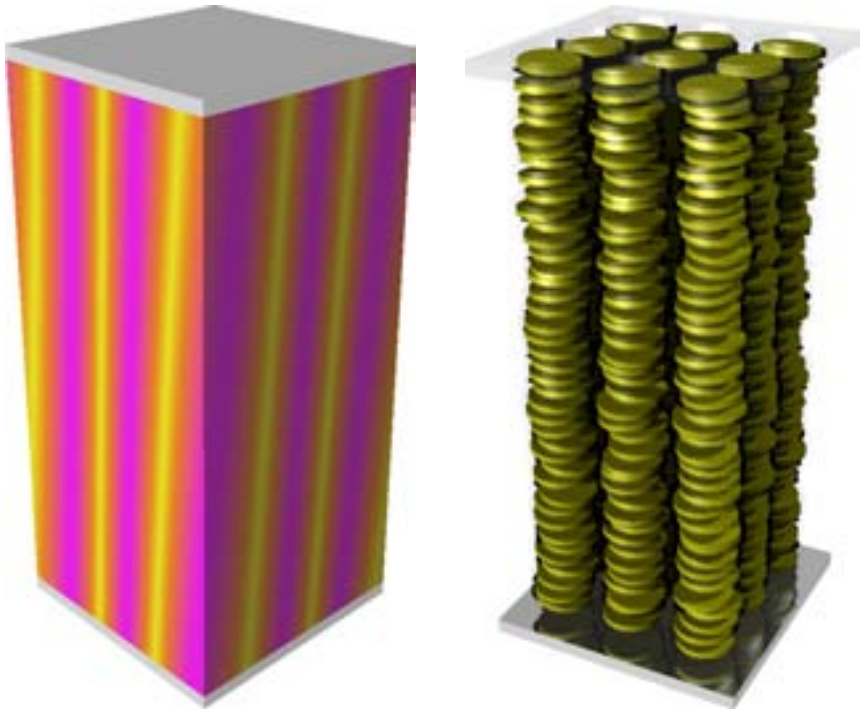
Blend solar cell



Competition between the interfacial area and the length of the percolation path

G. Yu and A. J. Heeger, **J. Appl. Phys.** (1995)
G. Yu, J. Gao, J. C Hummelen, F. Wudl, and A. J. Heeger, **Science** (1995)
J. J. M. Halls, C. A. Walsh et al **Nature** (1995)

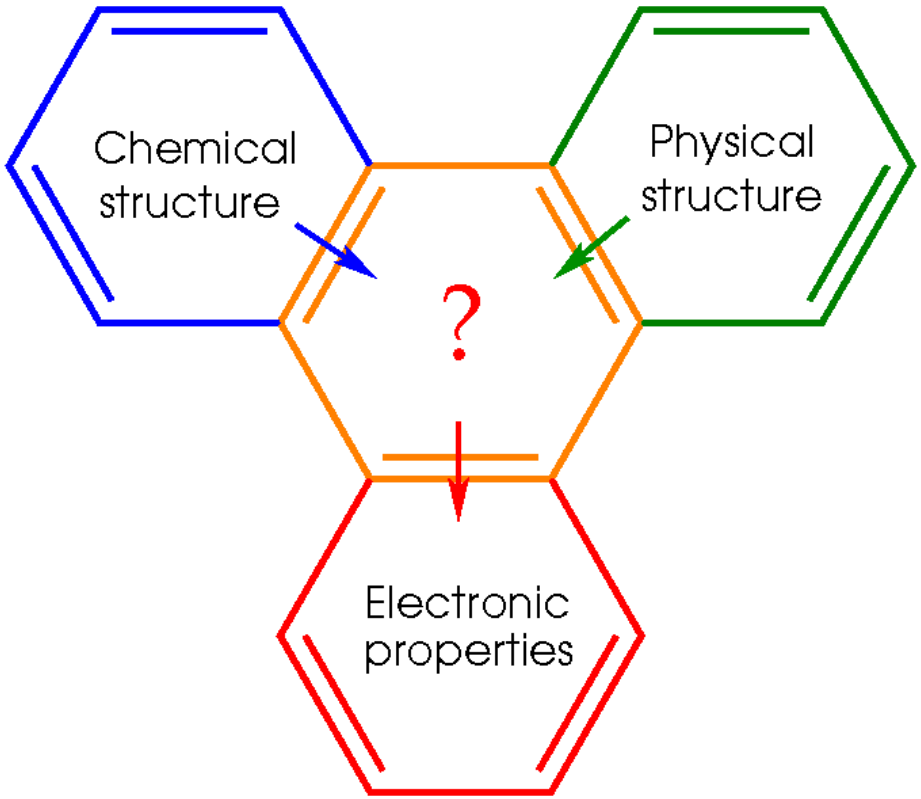
Self-assembly



(1) excitons are generated close to the interface; (2) there are uninterrupted pathways to the electrodes; (3) the phases are connected exclusively to the appropriate electrode

K. M. Coakley and M. D. McGehee, Appl. Phys. Lett. 83, 3380 (2003)
K. M. Coakley, Y. Liu, C. Goh, and M. D. McGehee, MRS Bull. 30, 37 (2005)
G. A. Buxton and N. Clarke **Phys Rev B** (2006)

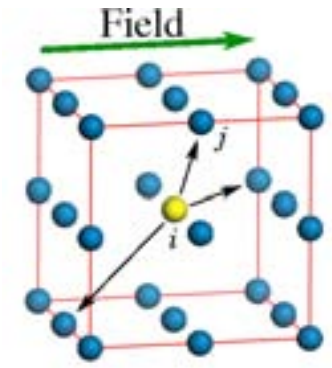
Structure-charge mobility relation



1. self-organization and large scale morphology
2. electronic properties: bandgap, alignment of levels
3. local molecular arrangment and **charge transport**

How to combine quantum and classical descriptions?

Gaussian disorder model

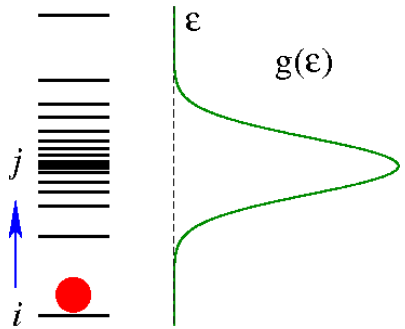


Transition probability to hop from i to j (Miller and Abrahams, 1960)

$$\omega_{ij} = \begin{cases} \nu_0 \exp(-2\alpha r_{ij}) \exp\left(-\frac{\epsilon_j - \epsilon_i}{k_B T}\right), & \epsilon_j > \epsilon_i \\ \nu_0 \exp(-2\alpha r_{ij}), & \epsilon_j < \epsilon_i \end{cases}$$

Gaussian distribution of energies: $g_e(\epsilon) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2}\right)$

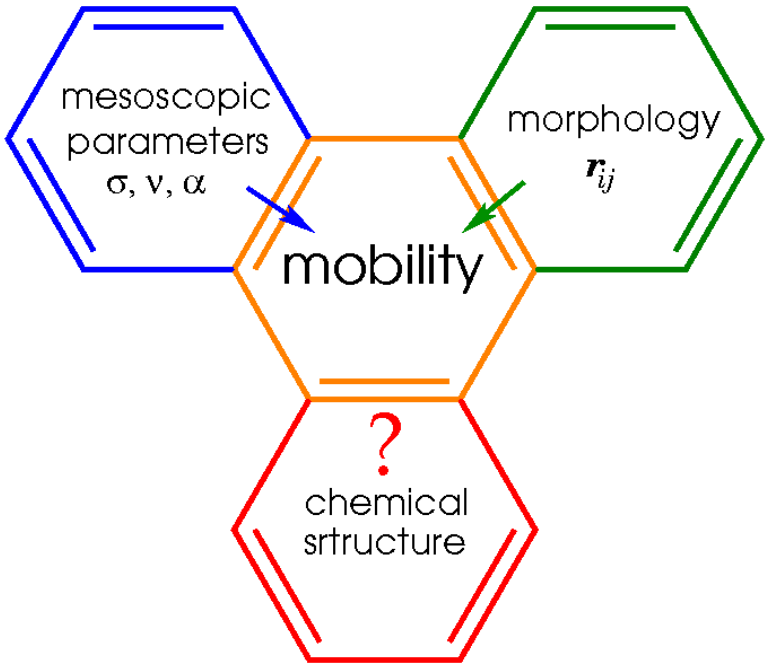
separations: $g_s(r_{ij}) = \frac{1}{\sqrt{2\pi}\Sigma} \exp\left(-\frac{r_{ij}^2}{2\Sigma^2}\right)$



No **analytical** solution - Kinetic Monte Carlo simulations are fitted to some impirical function.

A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960)

GDM mobility



$$\mu = \mu_0 \exp\left[-\left(\frac{2\sigma}{3k_B T}\right)^2\right] \times \exp\left[C_0\sqrt{F}\left(\left\{\frac{\sigma}{k_B T}\right\}^2 - \Sigma^2\right)\right]$$

μ_0 - mobility prefactor - related to the transfer integral J?

σ - energetic disorder - related to conjugation length, electrostatic potential?

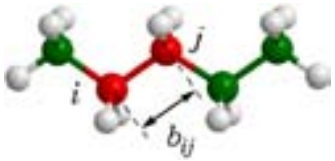
Σ - positional disorder - related to hopping distance, orientation?

GDM parameters can **quantify** differences in charge transport of different materials, but offer no way to **predict** them from chemical and physical structure

H. Bässler, Phys. Stat. Sol. B **175**, 15 (1993)

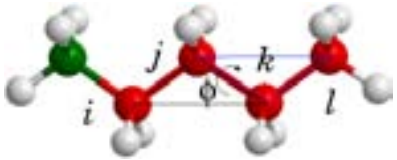
Force-field

Bonds

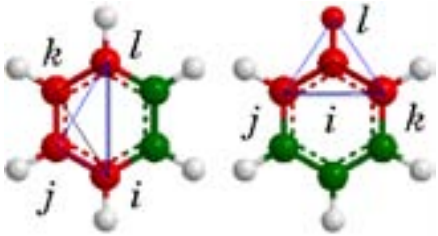


Angles

Torsions



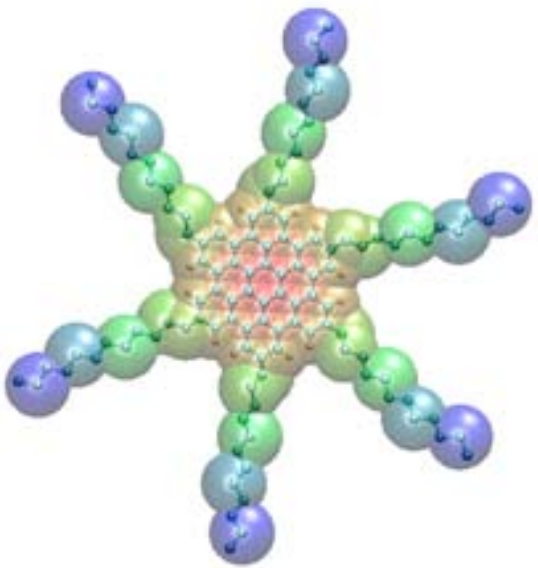
Improper dihedrals



$$
\begin{aligned}
U &= \sum_{\text{bonds}} \frac{1}{2} K_b \left(r - r_0\right)^2 \\
&+ \sum_{\text{angles}} \frac{1}{2} K_\theta \left(\theta - \theta_0\right)^2 \\
&+ \sum_{\text{dihedrals}} \sum_{n=1}^{3} \left[\frac{V_n}{2} + \left(1 + (-1)^{n+1} \cos n\phi\right) \right] \\
&+ \sum_{\text{impropers}} K_d \left(\psi - \psi_0\right)^2 \\
&+ \sum_i \sum_{j>i} \left[\frac{1}{4\pi\epsilon\epsilon_0} \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right\} \right]
\end{aligned}
$$

Goal: to match calorimetric, X-ray scattering, and NMR data.

Systematic coarse-graining



Bonded interactions The coarse-grained potential is a Boltzmann inversion of the corresponding probability density distribution. It is computed via Monte Carlo sampling of the atomistic structure of an isolated molecule.

$$P(\{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\}) = \prod_{i=1}^{N} P(\mathbf{x}_i).$$

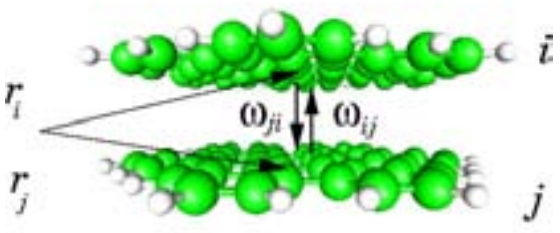
$$P(x_i) \sim \exp\left(-\frac{U(x_i)}{k_B T}\right).$$

The non-bonded potential Can be found by fitting RDFs for bonded interactions (iterative Boltzmann or force-matching)

$$U_{cg}^{nb} = \sum U_{ij}(\mathbf{r}_{ij}).$$

C. F. Abrams and K. Kremer **Macromolecules**(2003); F. Müller-Plathe, **ChemPhysChem** (2002)
S. Izvekov, A. Violi **J Chem Theory Comput** (2006); G. Voth **J Chem Theory Comput** (2006)

Marcus rates



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

λ - reorganization energy

$J_{ij} = \langle \Psi^i | \mathcal{H} | \Psi^j \rangle$ - transfer integral

$\Delta G_{ij} = \mathbf{E} \cdot \mathbf{r} + \Delta G_{ij}^{\mathrm{el}}$ - free energy difference between initial and final states

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R. A. Marcus, Rev. Mod. Phys. **65**, 599 (1993)
K. F. Freed and J. Jortner **J. Chem Phys.** (1970)

Reorganization Energy - typical values

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

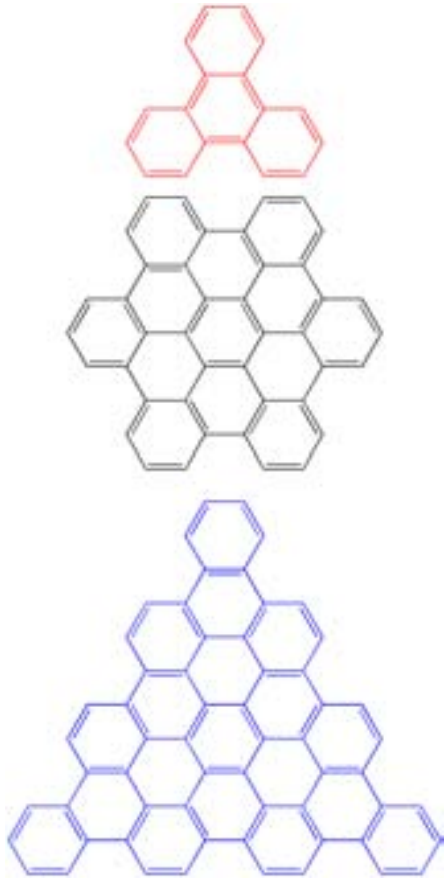


Table: Internal reorganization energies of typical discotics.

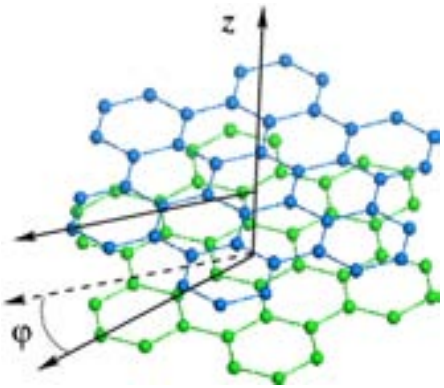
Geometry optimisation B3LYP/6-311++g(d,p).

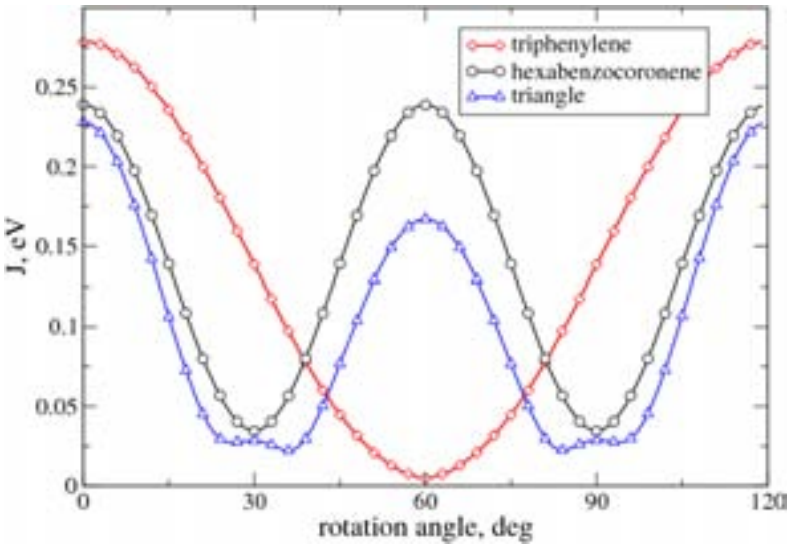
Compound	λ, eV
triphenylene	0.18
hexabenzocoronene	0.1
triangular PAH	0.09

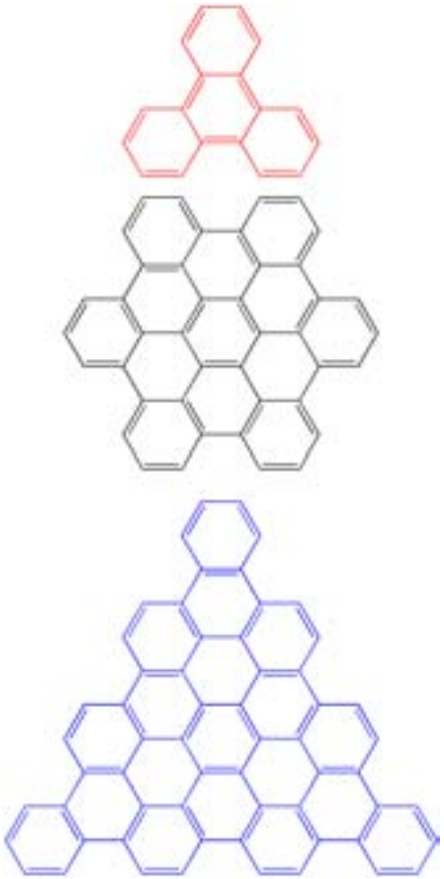
G. R. Hutchison, M. A. Ratner, and T. J. Marks, J. Am. Chem. Soc. **127**, 2339 (2005)

Transfer Integral J

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

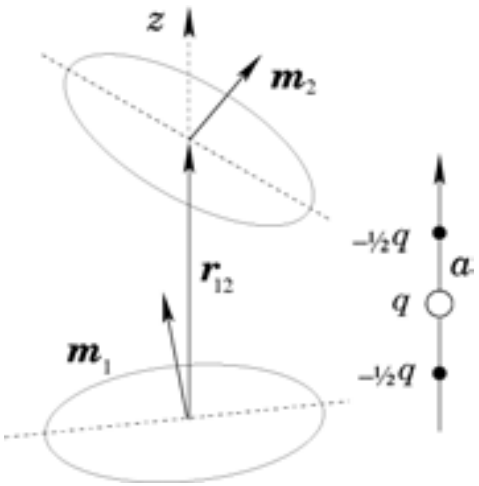






J. L. Bredas, et al Chem. Rev. **104**, 4971 (2004); J. L. Bredas, et al PNAS **99**, 5804 (2002)
J. Kirkpatrick, **Int. J. Quant. Chem.**, (2007); K. Senthilkumar, et al **J. Chem. Phys.** (2003)
E. F. Valeev, **J. Am. Chem. Soc.** (2006)

Energetic disorder (electrostatics and polarization)



Along the normal the π electrons form a linear quadrupole and the molecule is far less polarizable than in the molecular plane

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

Electrostatic case [interaction of a linear quadrupole Q with a charge]

$$\Delta G_{\mathrm{el}} = \frac{3eQ}{16\pi\epsilon_0 r_{12}^3}(\cos^2\theta_1 - \cos^2\theta_2)$$

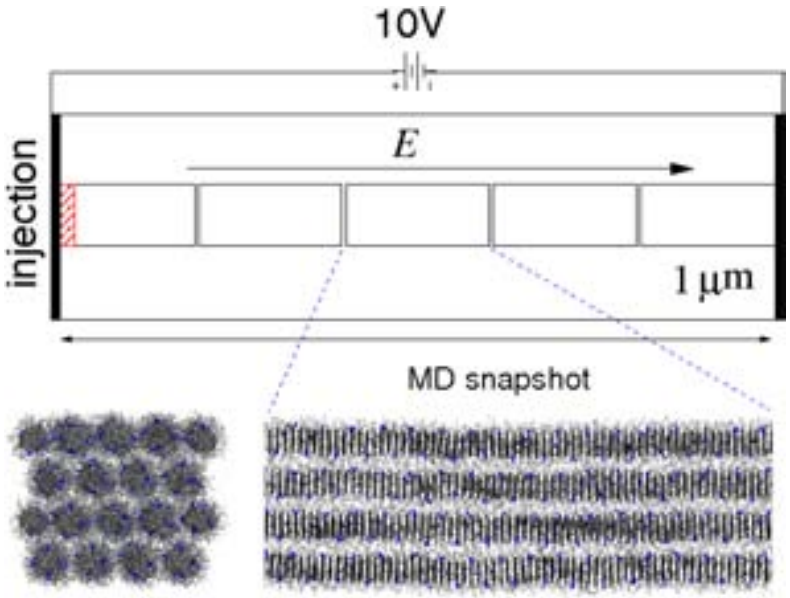
Polarization case [interaction of a charge with a polarizable dipole, $\alpha = 0.7\text{Å}^3$]

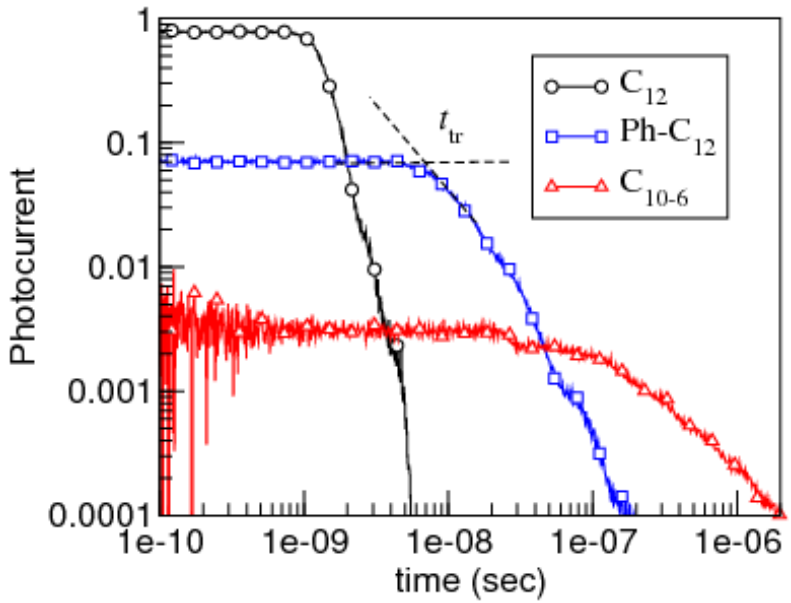
$$\Delta G_{\mathrm{pol}} = \alpha\left(\frac{e}{4\pi\epsilon_0 r_{12}^2}\right)^2(\sin^4\theta_1 - \sin^4\theta_2)$$

Only **out-of-plane** fluctuations contribute to energetic disorder.
Disorder is intrinsically greater for negative charges than for positive ones.

J. Kirkpatrick, V. Marcon, K. Kremer, J. Nelson, D. Andrienko, *J. Chem. Phys.* **129**, 094506 (2008)

KMC simulations of time-of-flight experiments

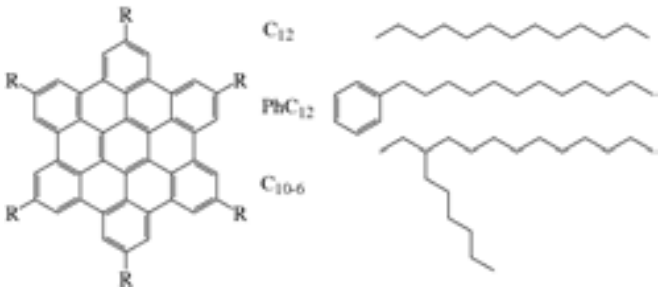


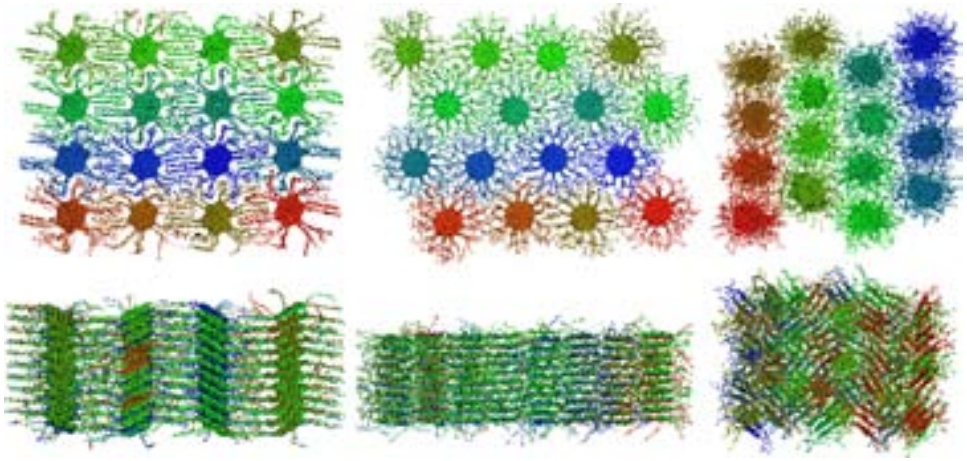


- inject a charge
- pick a neighboring site j at random, weighting by its rate ω_{ij}
- advance waiting time by $t_i = \frac{-\log \xi}{\sum_{j=0}^{N} \omega_{ij}}$, where ξ is a random number.

J Nelson and R Chandler **Coord. Chem. Reviews** (2004)
J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, and D. Andrienko, **Phys. Rev. Lett.** (2007)
D. Andrienko, J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, **Phys. Stat. Sol. B** (2008)

Derivatives of hexabenzocoronenes

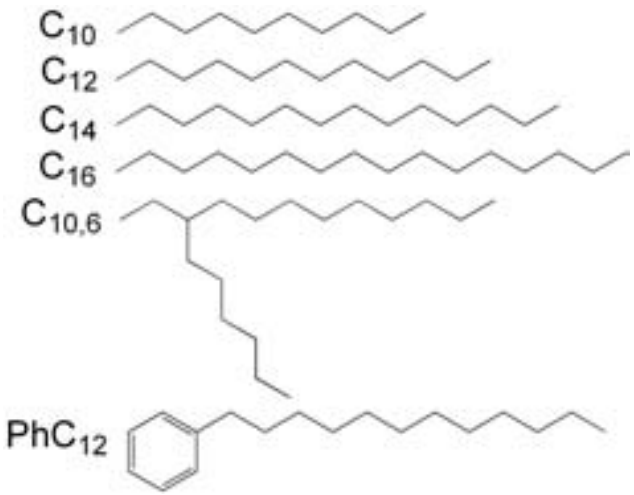


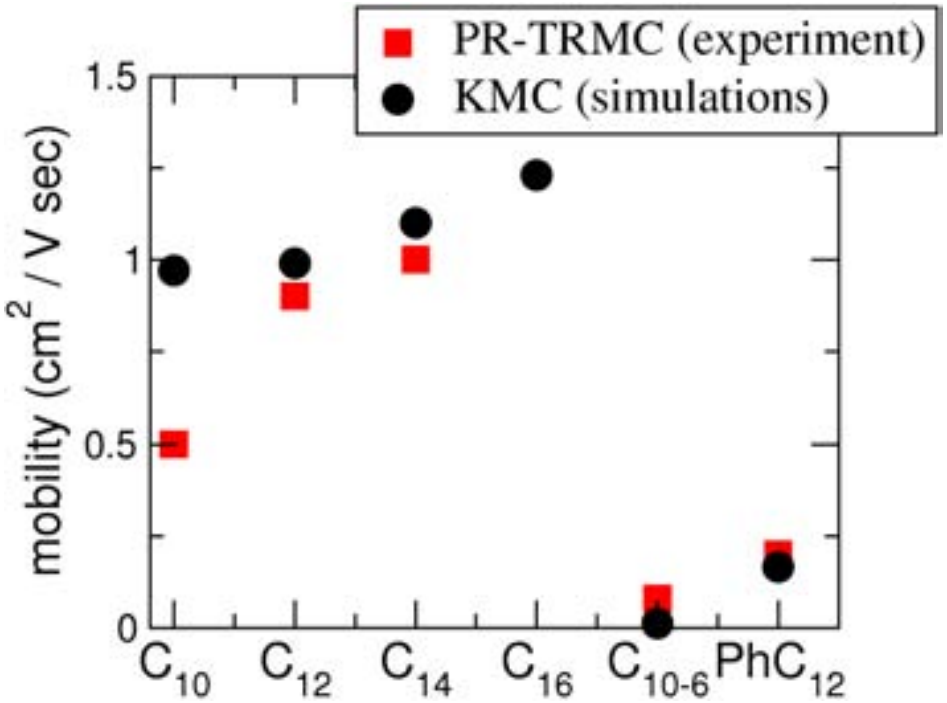


Influence of chemical structure and morphology on the charge carrier mobility?

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

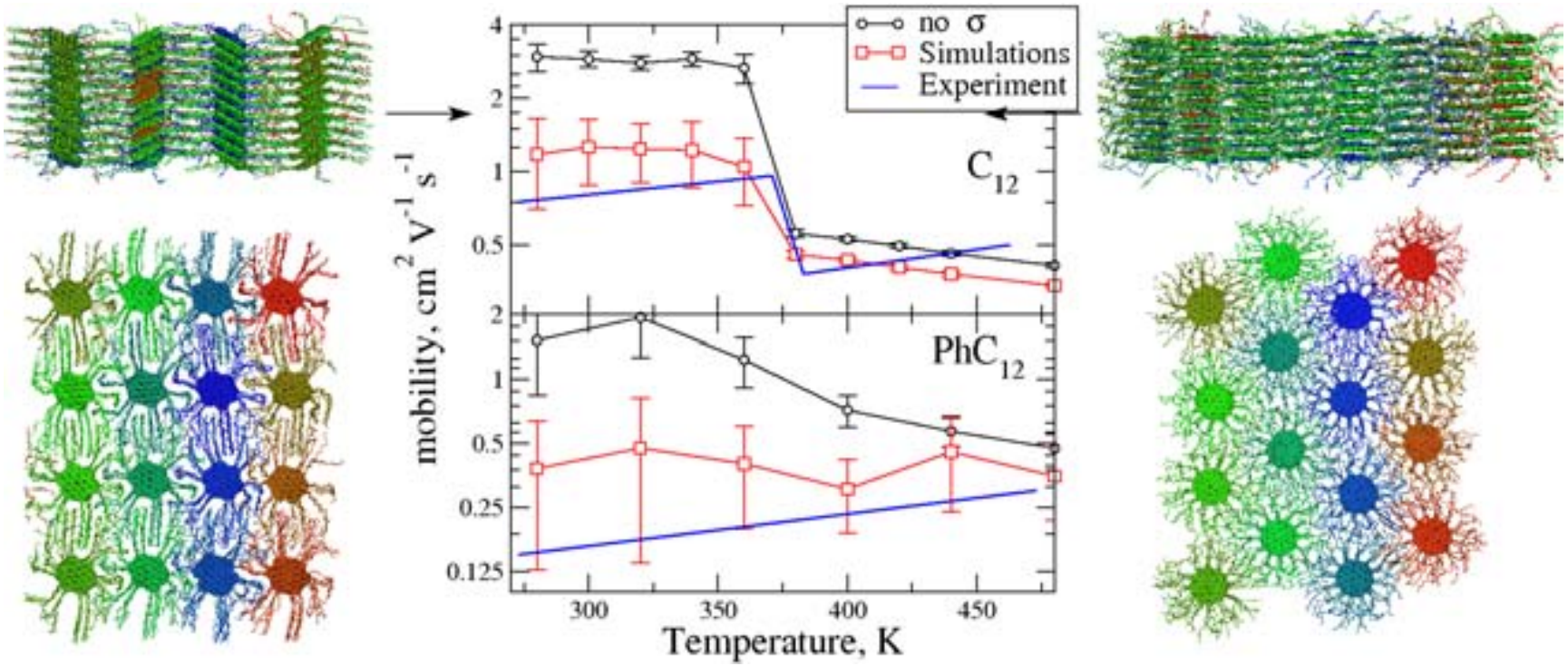
Side chain dependence





J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, and D. Andrienko, Phys. Rev. Lett. **98**, 227402 (2007)
D. Andrienko, J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, **Phys. Stat. Sol. B,** 2008

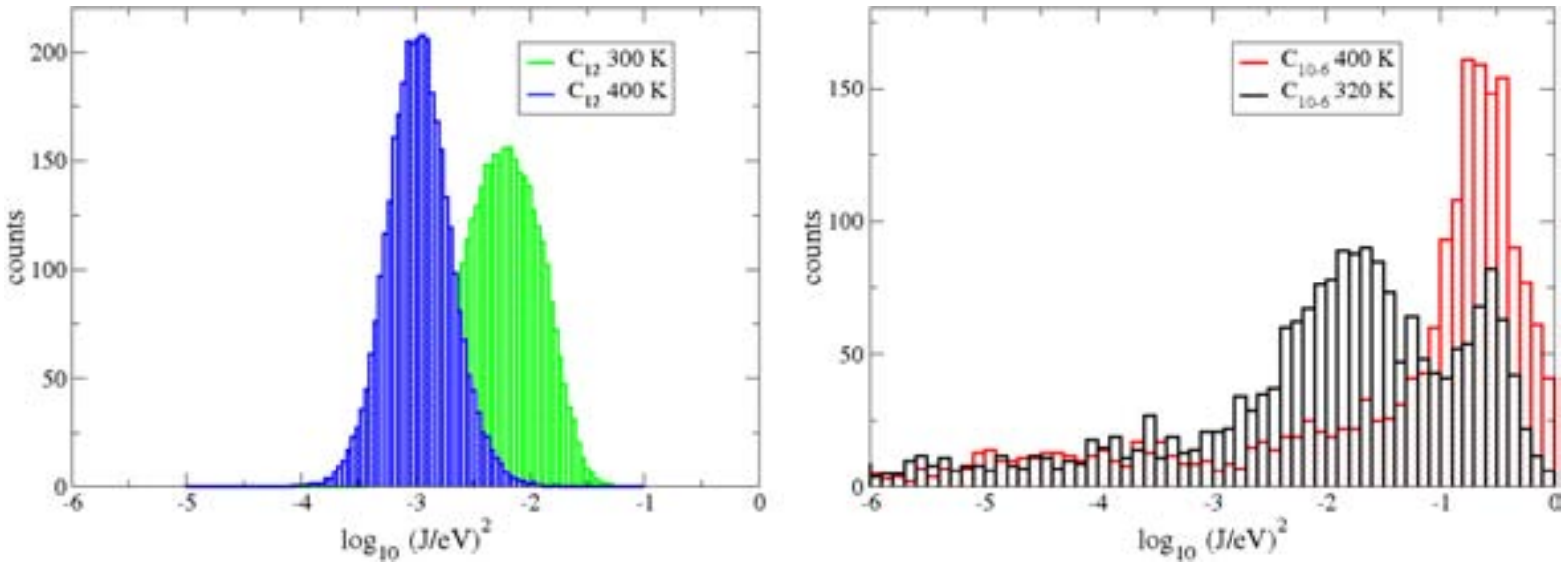
Temperature dependence



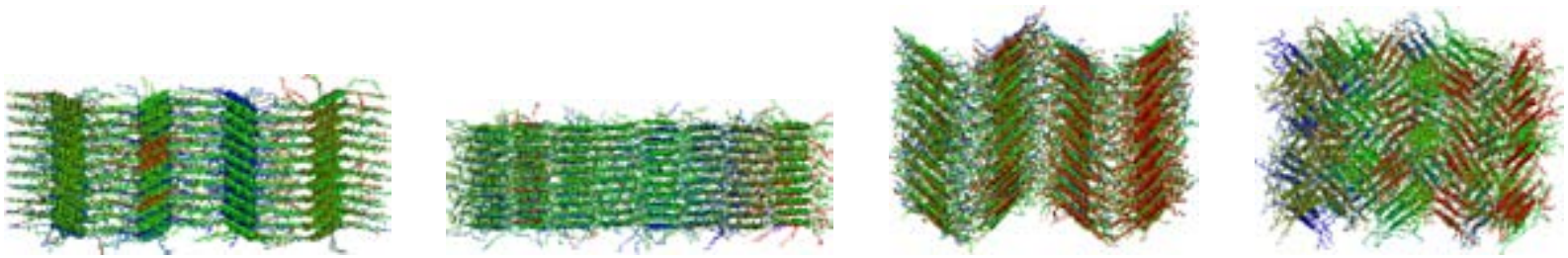
Herringbone phase has better azimuthal register of molecules

V. Marcon, T. Vehoff, J. Kirkpatrick, C. Jeong, D. Yoon, K. Kremer, D. Andrienko, *J. Chem. Phys.* **129**, 094505 (2008)
J. Kirkpatrick, V. Marcon, K. Kremer, J. Nelson, D. Andrienko, *J. Chem. Phys.* **129**, 094506 (2008)

Distributions of Transfer Integrals

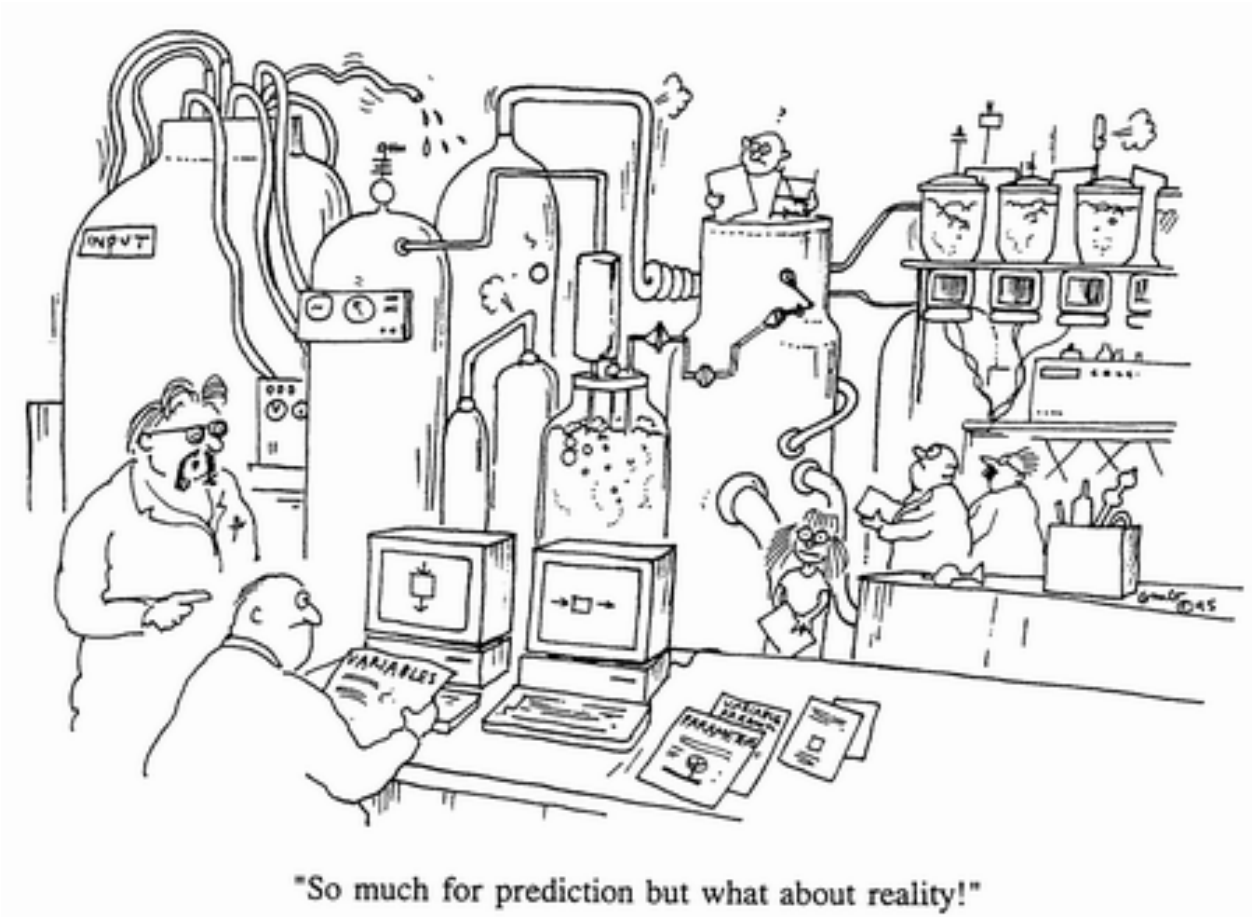


Frequency plots of the logarithm of the transfer integral squared. a) herringbone (300 K) and hexagonal (400 K) phases of the systems with C_{12} side chains. b) herringbone (320K) and hexagonal (400 K) of HBC with dove-tail side chains.



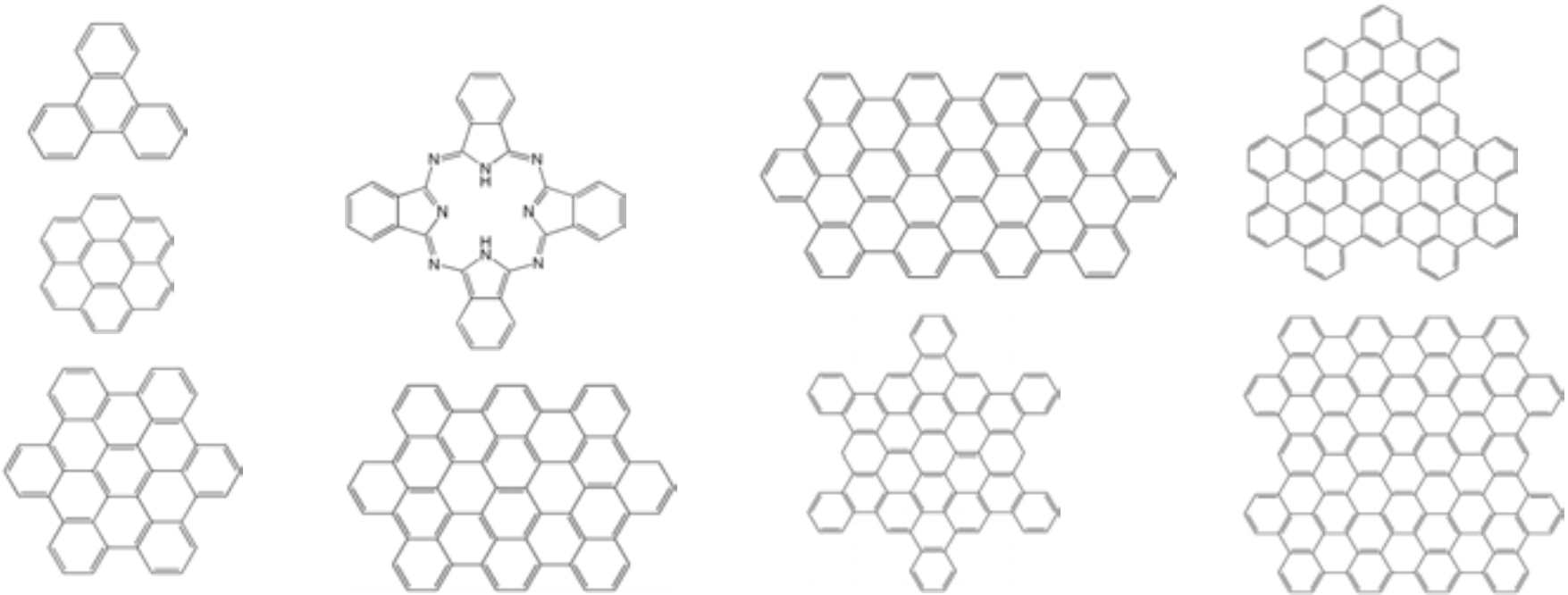
J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, and D. Andrienko, **Phys. Rev. Lett.** (2007)
D. Andrienko, J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, **Phys. Stat. Sol. B**, (2008)

Collaboration with the organic chemistry group...



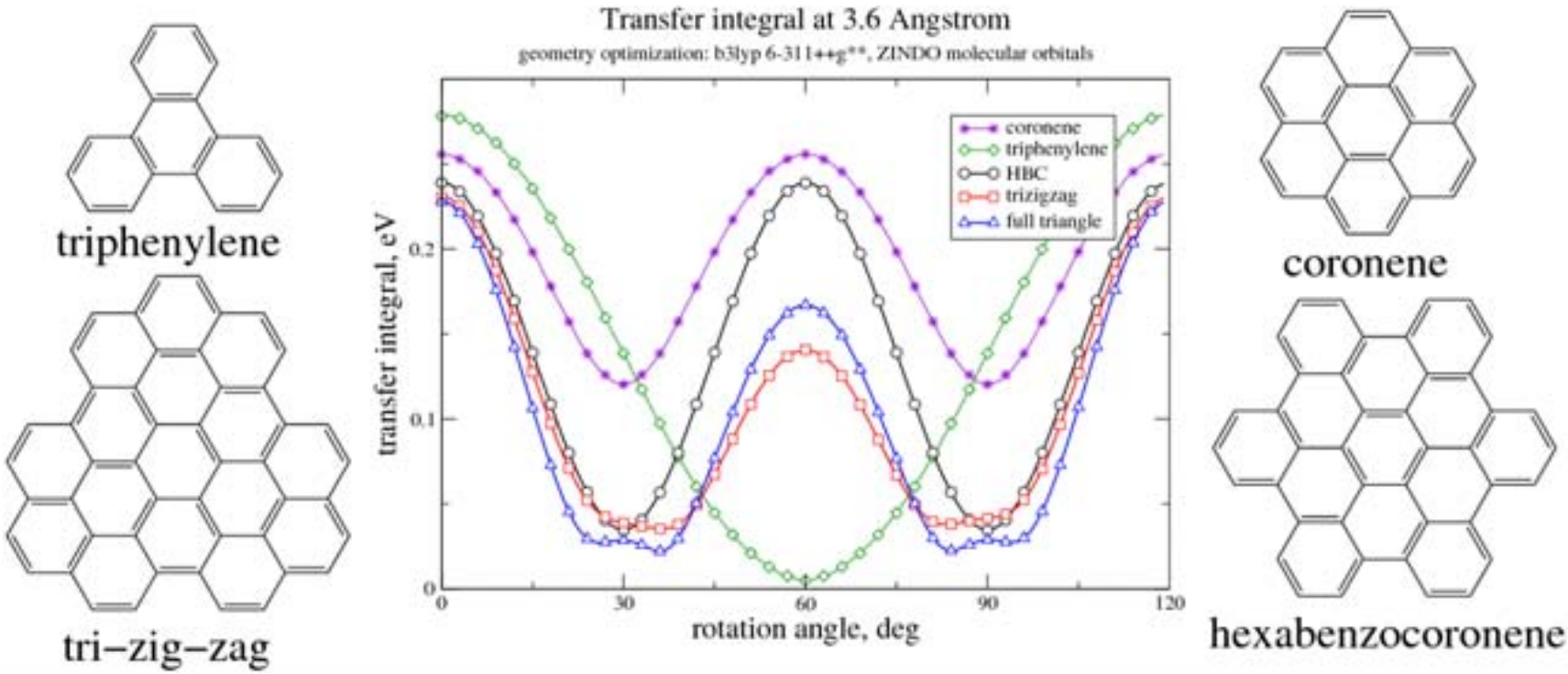
"So much for prediction but what about reality!"

Triphenylenes, hexabenzocoronenes, phthalocyanines ...



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

Transfer Integral J



Maximum of the transfer integral (hoping rate) is in the face-to-face geometry and in a 60 deg twisted arrangement of neighbors.

Compound design

- Triangularly-shaped core

X. Feng, W. Pisula, V. Marcon, J. Kirkpatrick, F. Grozema, K. Kremer, K. Müllen, D. Andrienko, submitted (2008)

Compound design

- Triangularly-shaped core
- The core can provide 60 deg twist, due to steric repulsion

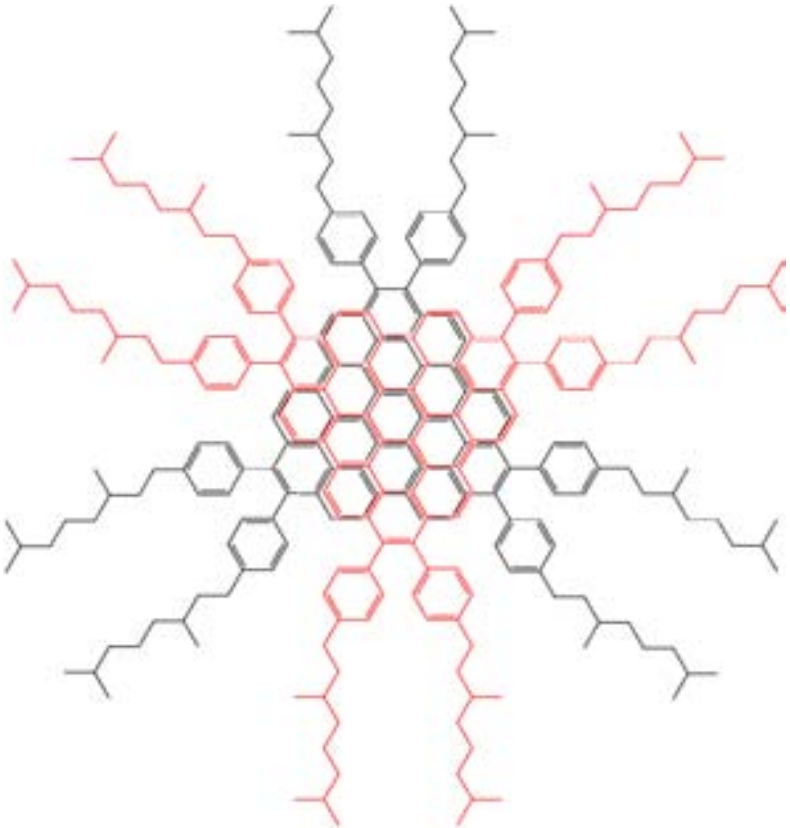
X. Feng, W. Pisula, V. Marcon, J. Kirkpatrick, F. Grozema, K. Kremer, K. Müllen, D. Andrienko, submitted (2008)

Compound design

- Triangularly-shaped core
- The core can provide 60 deg twist, due to steric repulsion
- Bulky side groups - to lock the azimuthal rotation

X. Feng, W. Pisula, V. Marcon, J. Kirkpatrick, F. Grozema, K. Kremer, K. Müllen, D. Andrienko, submitted (2008)

Compound design



- Triangularly-shaped core
- The core can provide 60 deg twist, due to steric repulsion
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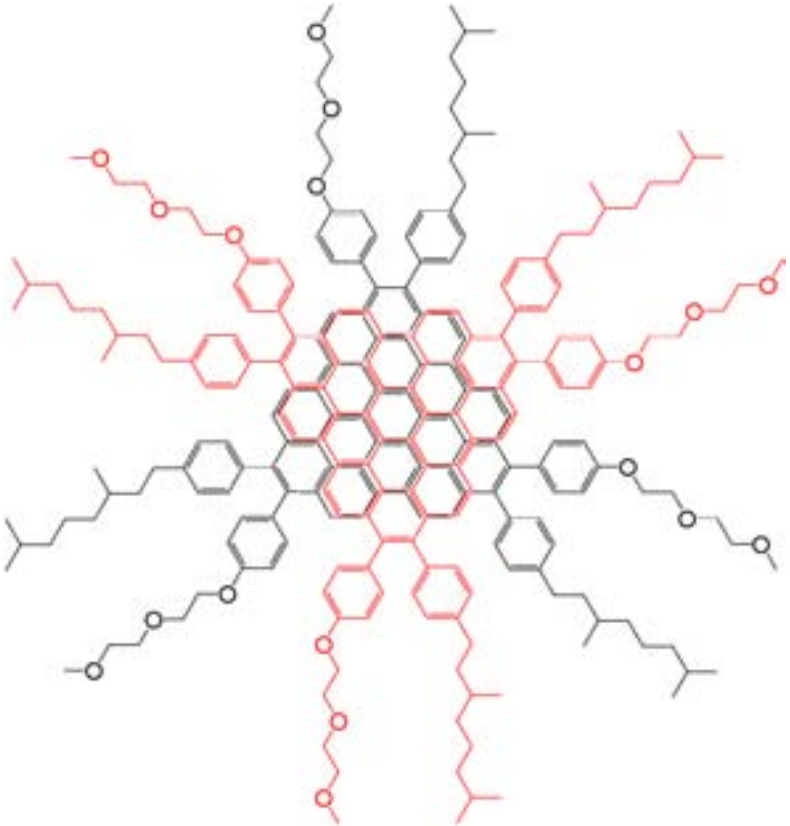
- Side chains to make the compound soluble

X. Feng, W. Pisula, V. Marcon, J. Kirkpatrick, F. Grozema, K. Kremer, K. Müllen, D. Andrienko, submitted (2008)

Compound design

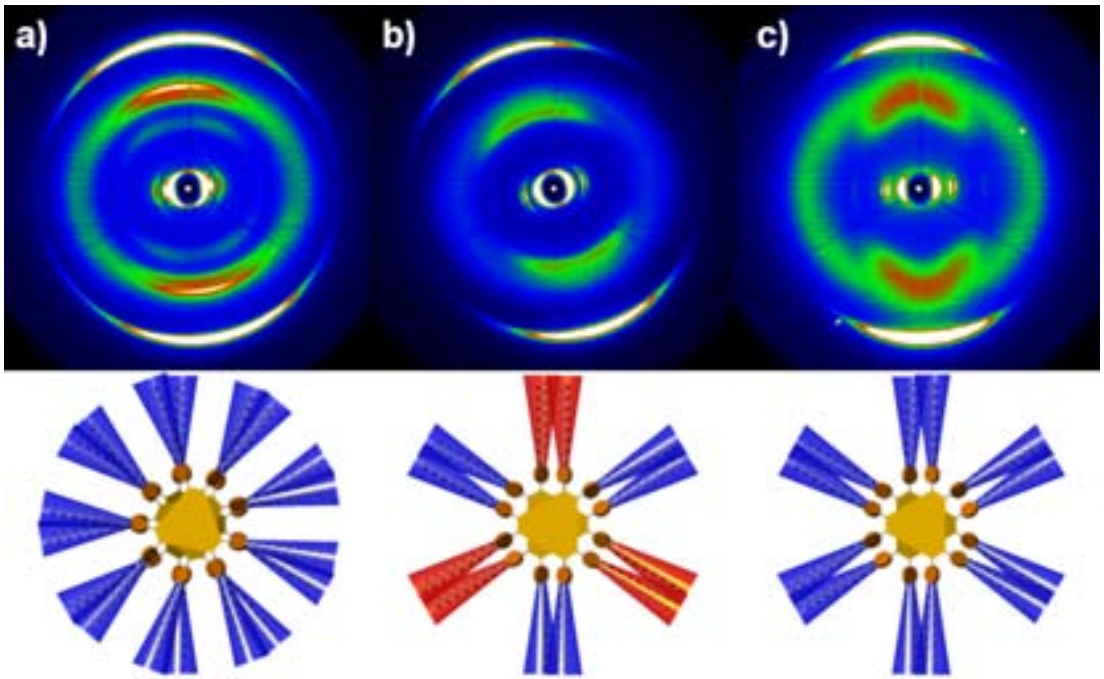


- Triangularly-shaped core
- The core can provide 60 deg twist, due to steric repulsion
- Bulky side groups - to lock the azimuthal rotation
- Side chains to make the compound soluble
- Polar side chains - to further stabilize the twist

X. Feng, W. Pisula, V. Marcon, J. Kirkpatrick, F. Grozema, K. Kremer, K. Müllen, D. Andrienko, submitted (2008)

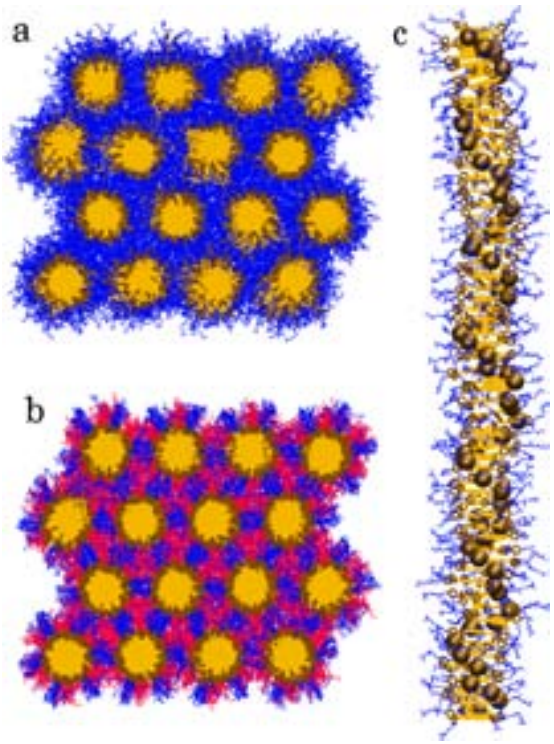
Experimental data

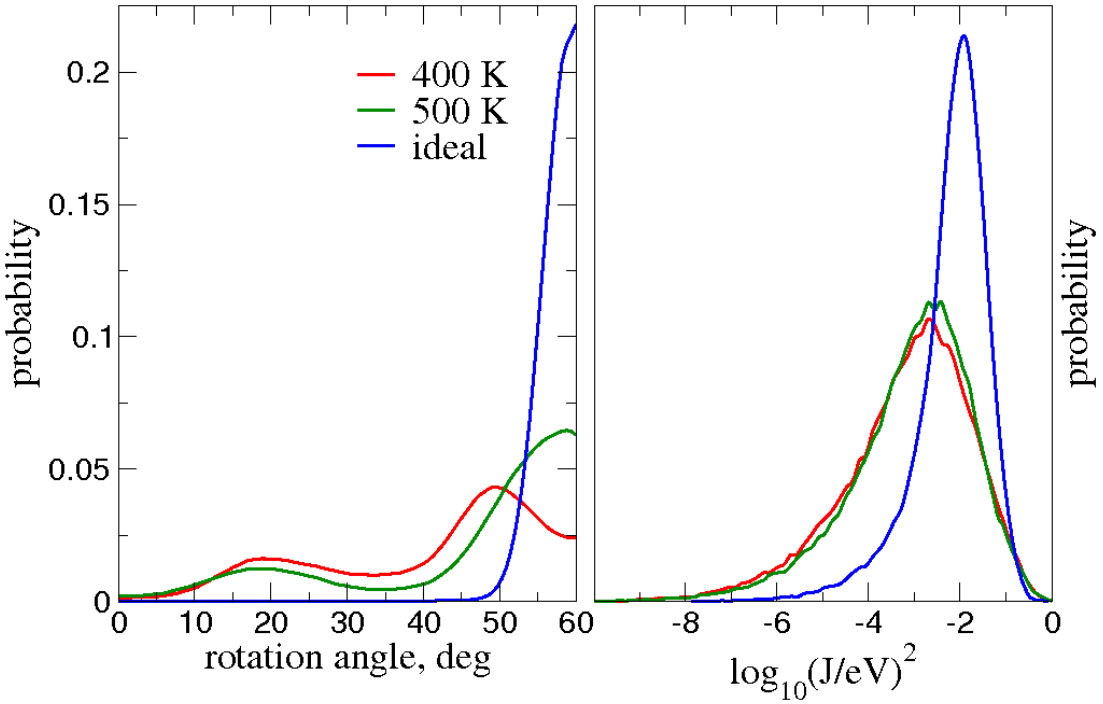
X. Feng, W. Pisula, and K. Müllen - synthesis and characterization



X. Feng, J. Wu, M. Ai, W. Pisula, L. Zhi, J. P. Rabe, and K. Müllen, *Angew. Chem. Int. Ed* 2007
X. Feng, W. Pisula, V. Marcon, J. Kirkpatrick, F. Grozema, K. Kremer, K. Müllen, D. Andrienko (2008)

Simulations

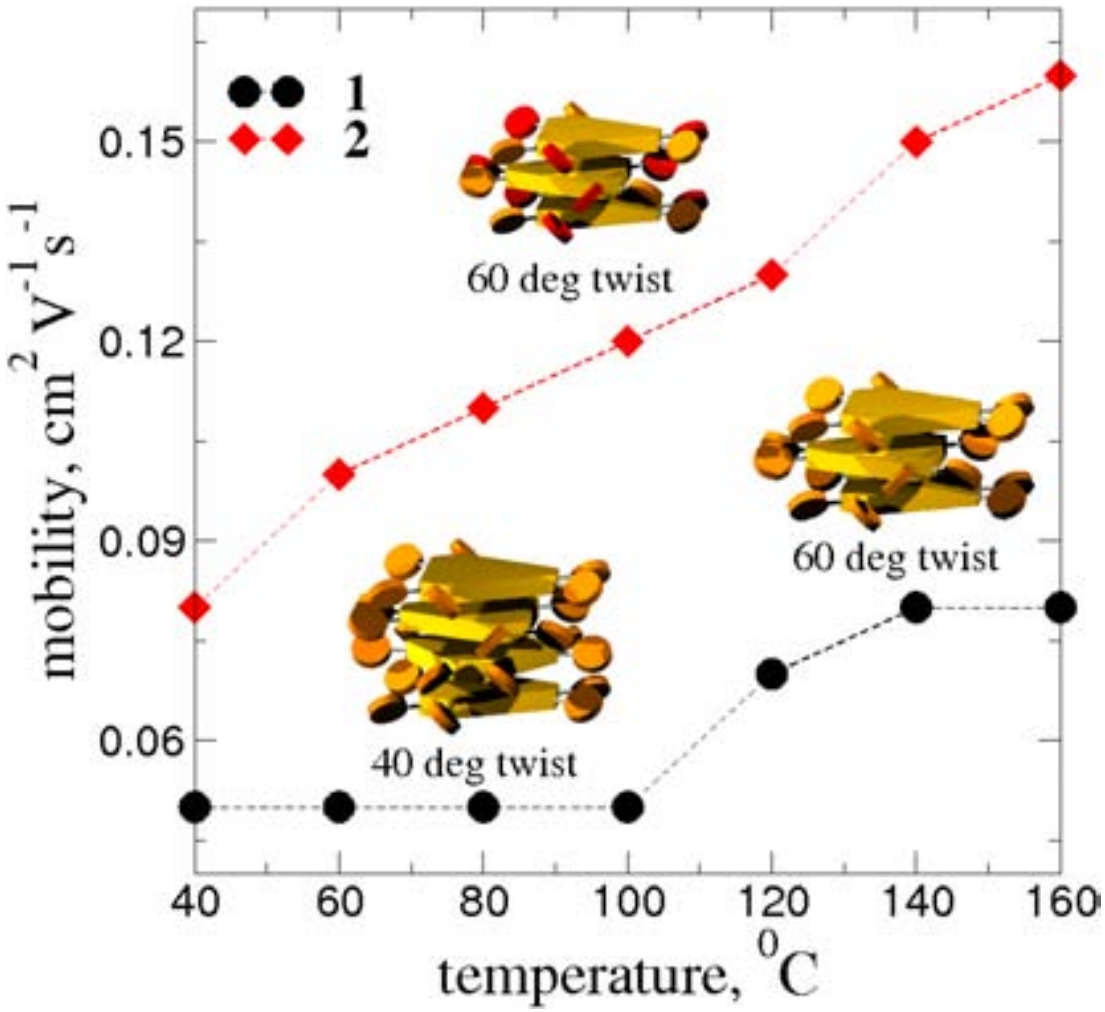




Distribution functions of the azimuthal angle and transfer integral between nearest neighbors.

X. Feng, W. Pisula, V. Marcon, J. Kirkpatrick, F. Grozema, K. Kremer, K. Müllen, D. Andrienko, Nature Materials (2008)

PR-TRMC mobility



PR-TRMC mobilities vs temperature

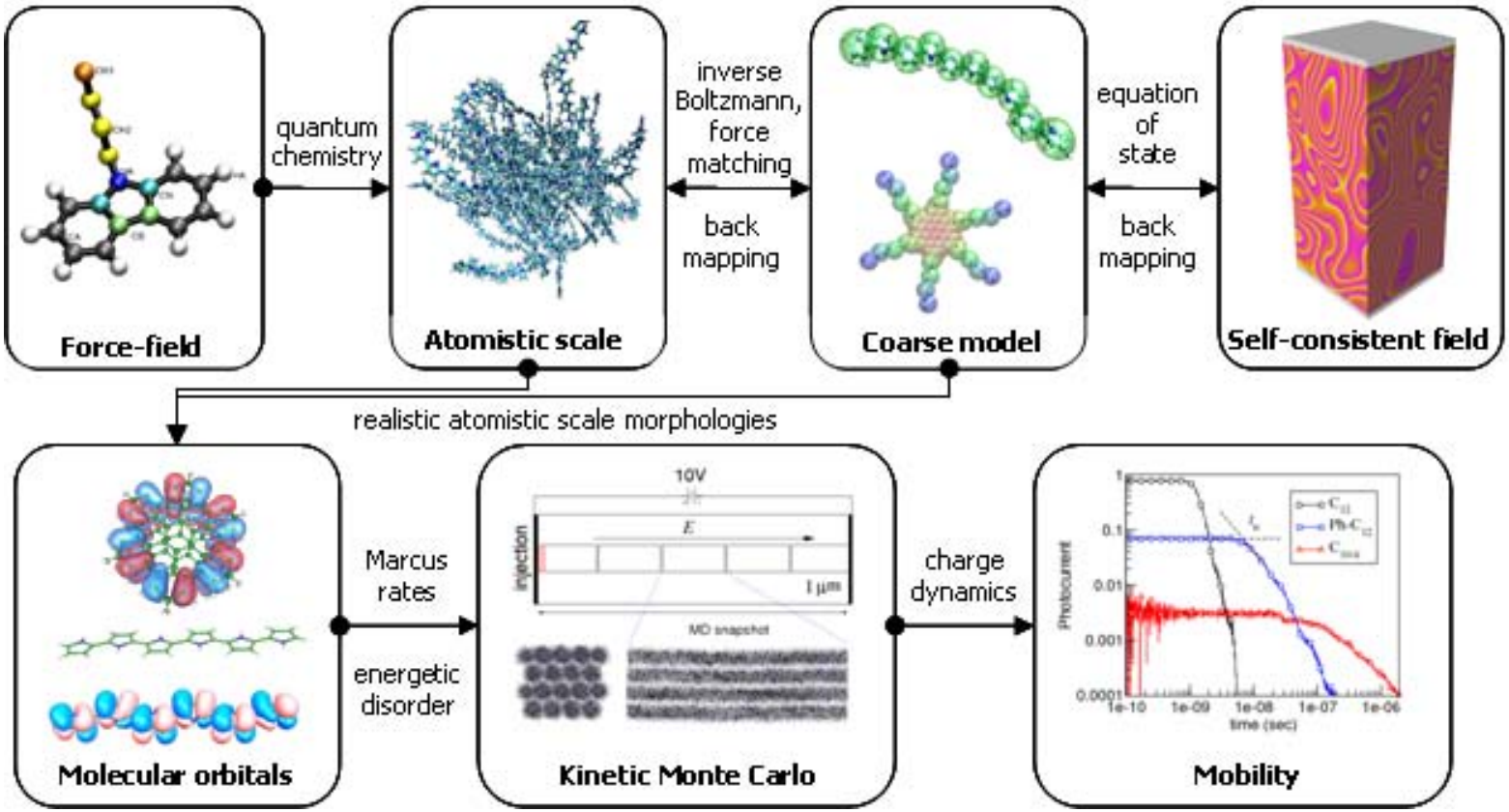
V. Marcon (MPIP)
F. Grozema (TU Delft)

X. Feng, W. Pisula, V. Marcon, J. Kirkpatrick, F. Grozema, K. Kremer, K. Müllen, D. Andrienko, Nature Materials (2008)

Summary and software package

csgth.mpip-mainz.mpg.de

c++, test suite, svn, wiki, bug tracker



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- A. Troisi (University of Warwick)
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