

# Charge transport in discotic liquid crystals

Denis Andrienko

Max Planck Institute for Polymer Research

SANDIA National Laboratory  
Albuquerque, 6 March 2008



# Max Planck Institute for Polymer Research

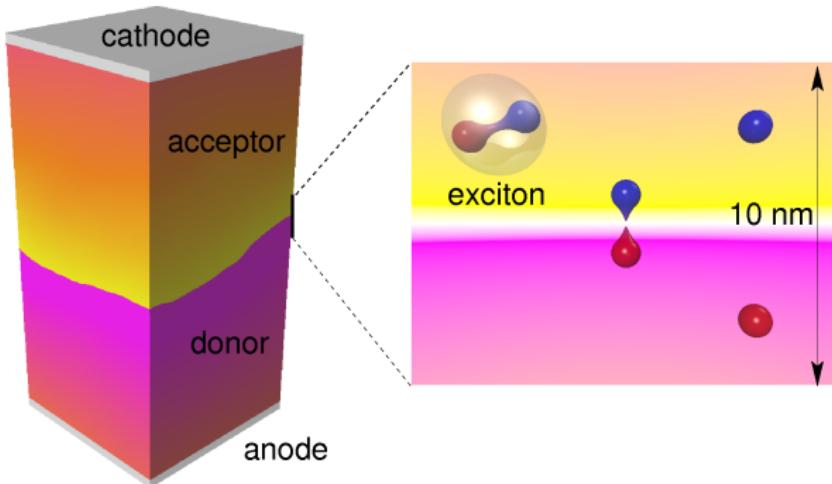


Location: Mainz, Germany. Founded 1983, 450-500 employees [ca 300 researchers]. Annual budget 24 Mio Euro, 330 papers/year. 6 departments (synth. chemistry, functional materials, theory and simulations, NMR, biomaterials, surfaces and interfaces)





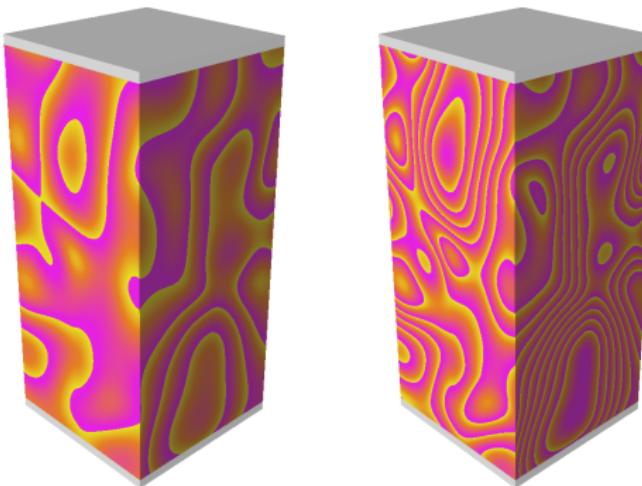
# Solar Cell Prototype



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



charge generation throughout the whole volume **but** bottlenecks prohibit free charges from reaching the electrodes

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

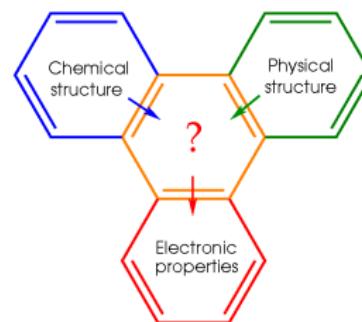
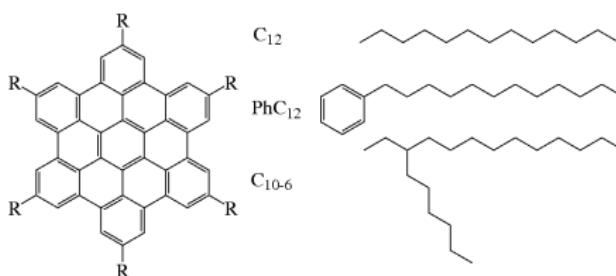
G. Yu and A. J. Heeger, *J. Appl. Phys.* (1995)

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)



# Derivatives of hexabenzocoronenes



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

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)











## Reorganization Energy

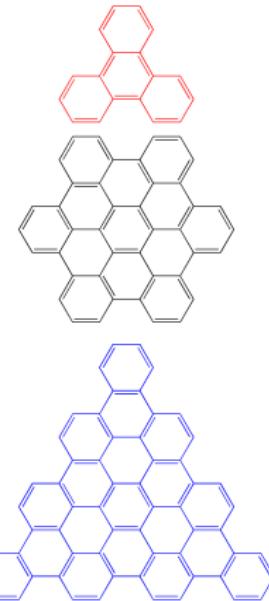
## Reorganization Energy - typical values

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

Table: Internal reorganization energies of typical discotics.

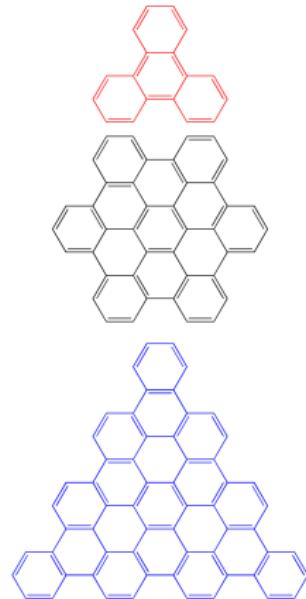
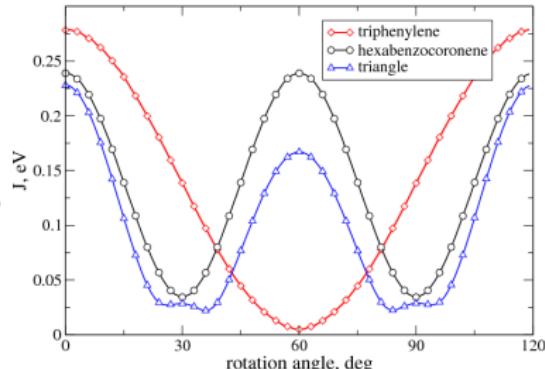
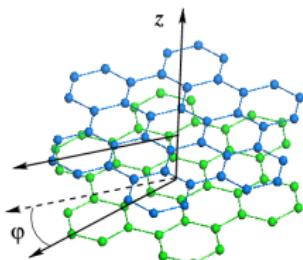
Geometry optimisation B3LYP/6-311++g(d,p).

Compound	$\lambda$ , 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

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

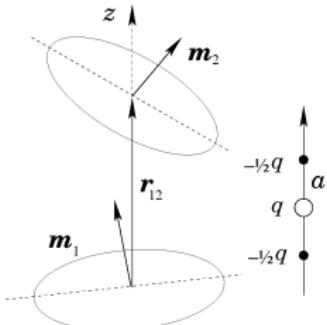


J. L. Bredas, et al Chem. Rev. **104**, 4971 (2004); J. L. Bredas, et al PNAS **99**, 5804 (2002)

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  $\pi$  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]

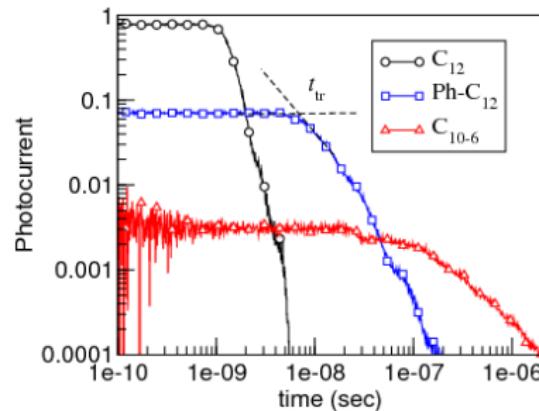
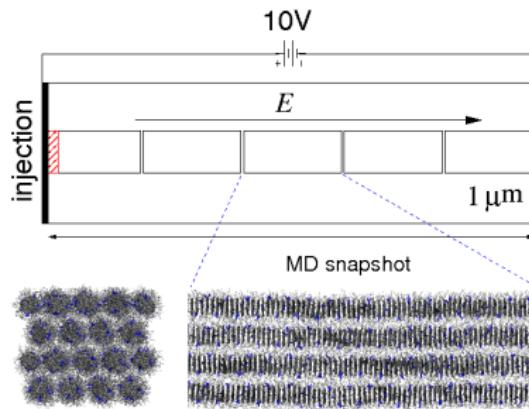
$$\Delta G_{el} = \frac{3eQ}{16\pi\epsilon_0 r_{12}^3} (\cos^2 \theta_1 - \cos^2 \theta_2)$$

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

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

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

# KMC simulations of time-of-flight experiments



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

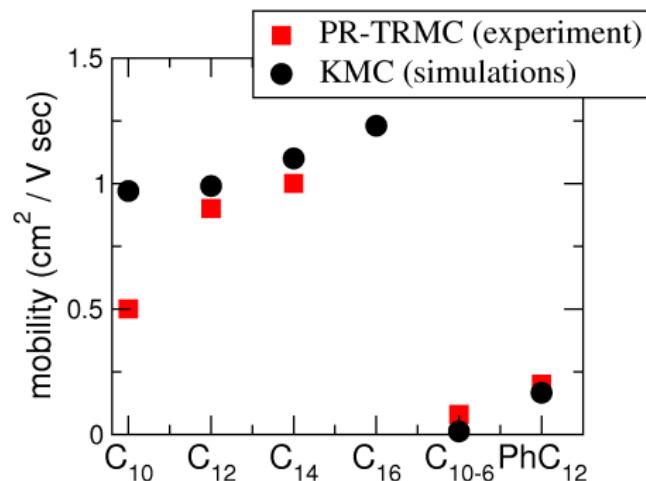
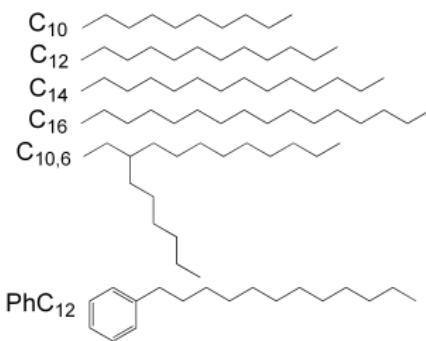
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J Nelson and R Chandler *Coord. Chem. Reviews* (2004)

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)

# Side chain dependence

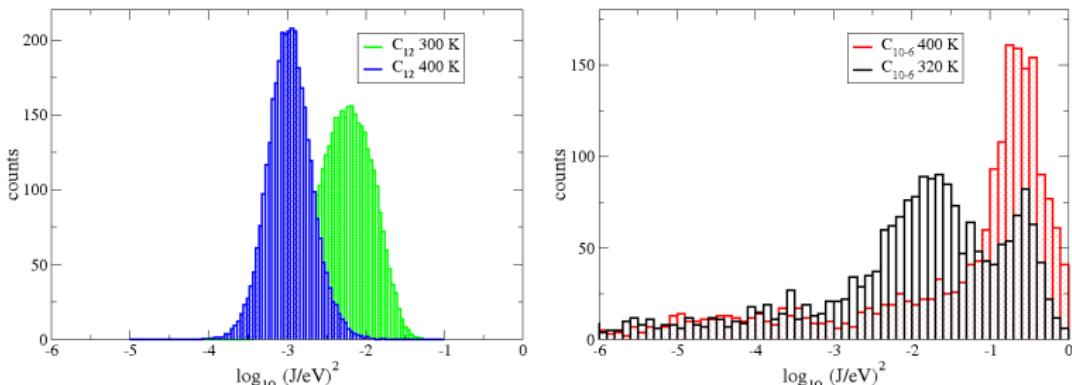



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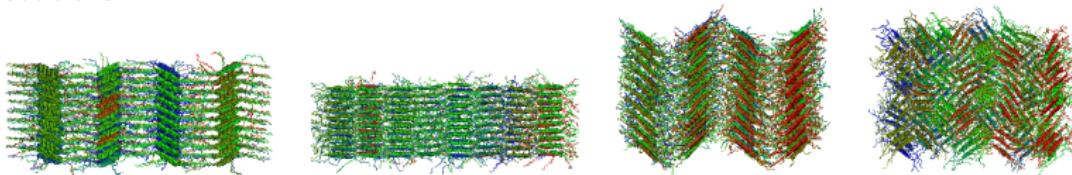
J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, and D. Andrienko, Phys. Rev. Lett. **98**, 227402 (2007)  
 D. Andrienko, J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, Phys. Stat. Sol. **B**, 2008

## Kinetic Monte Carlo

## Distributions of Transfer Integrals



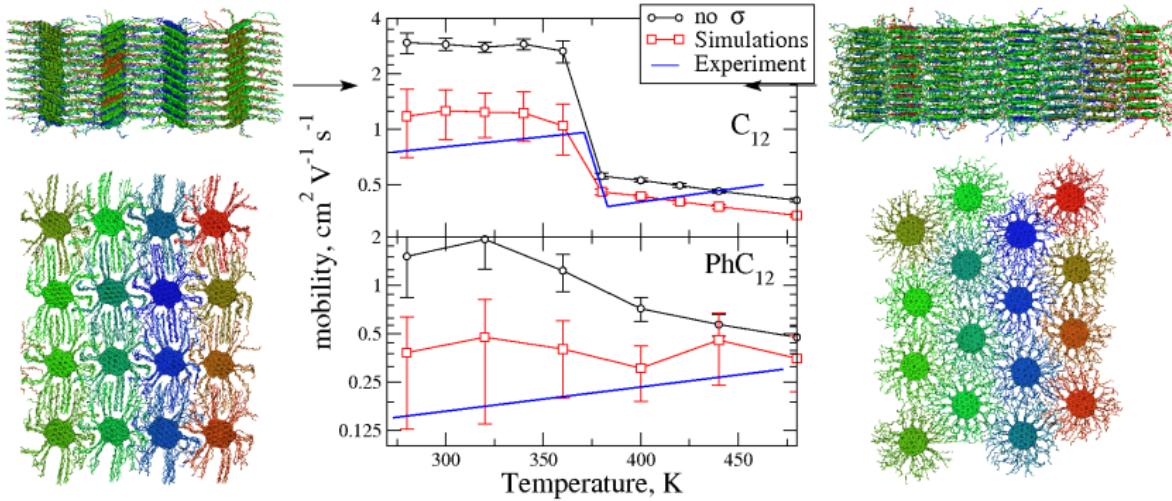
Frequency plots of the logarithm of the transfer integral squared. a) herringbone (300 K) and hexagonal (400 K) phases of the systems with  $C_{12}$  side chains. b) herringbone (320K) and hexagonal (400 K) of HBC with dove-tail side chains.



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)

# Temperature dependence



Change in mobility is due to better azimuthal register of the molecules

J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, D. Andrienko (2008)

# What do we learn?

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**M**orphology determines the distribution of hoping rates

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**I**mportant: azimuthal register of neighbors

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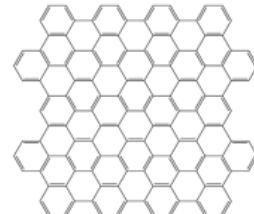
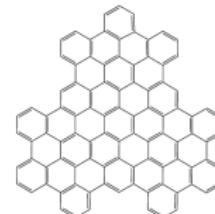
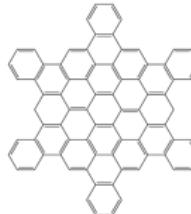
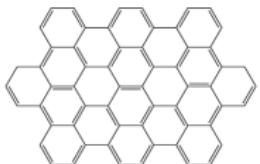
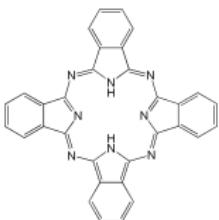
**P**ure 1D transport - the tail of small  $J$  determines the mobility

**I**mportant: azimuthal register of neighbors

**P**resence of energetic disorder is due to molecular tilting and affects electron and hole mobilities in a different way

## Discotic liquid crystals

## Triphenylenes, hexabenzocoronenes, phthalocyanines ...



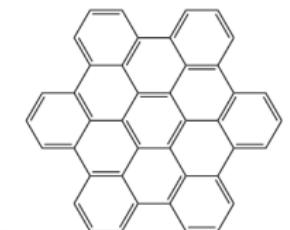
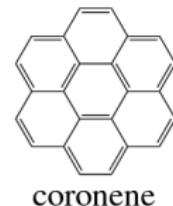
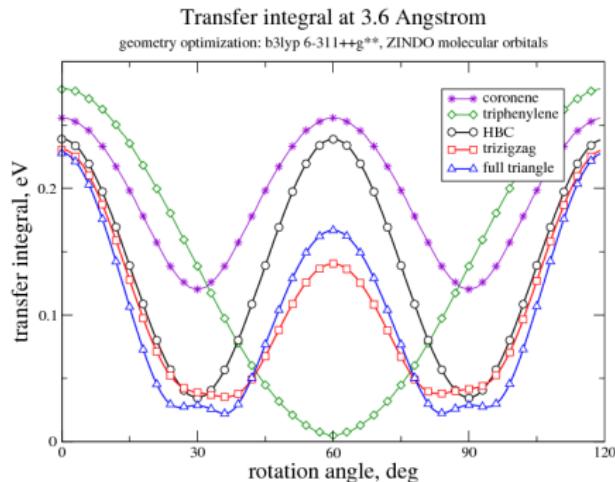
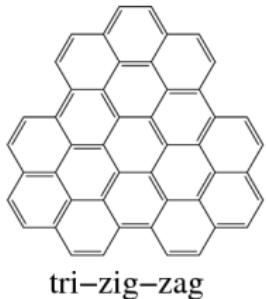
A. M. van de Graats et al, **Advanced Materials** 1999

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

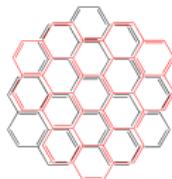
- Triangularly-shaped core



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

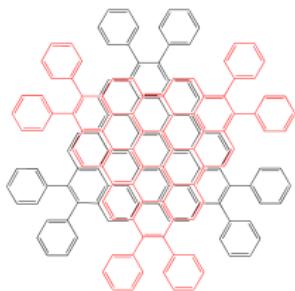
# Compound design

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



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

# Compound design

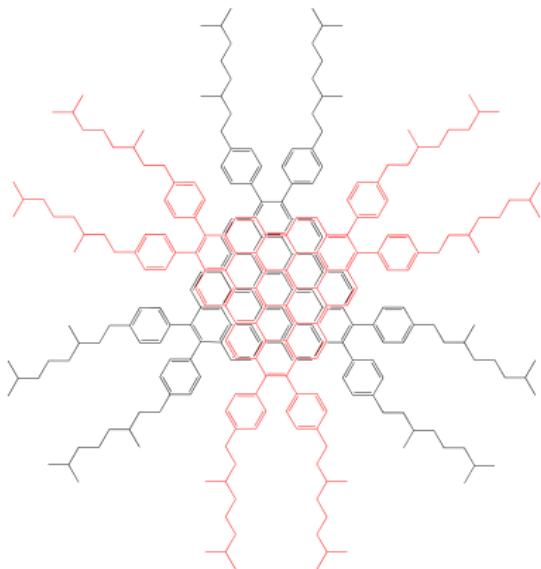


- Triangularly-shaped core
- The core can provide 60 deg twist, due to steric repulsion
- Bulky side groups - to lock the azimuthal rotation

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

## Triangular-shaped PAH

## Compound design



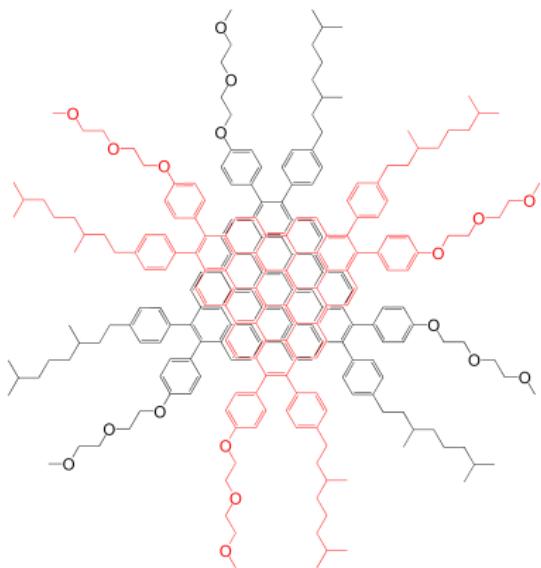
- Triangularly-shaped core
- The core can provide 60 deg twist, due to steric repulsion
- Bulky side groups - to lock the azimuthal rotation
- Side chains to make the compound soluble

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

## Triangular-shaped PAH

## 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

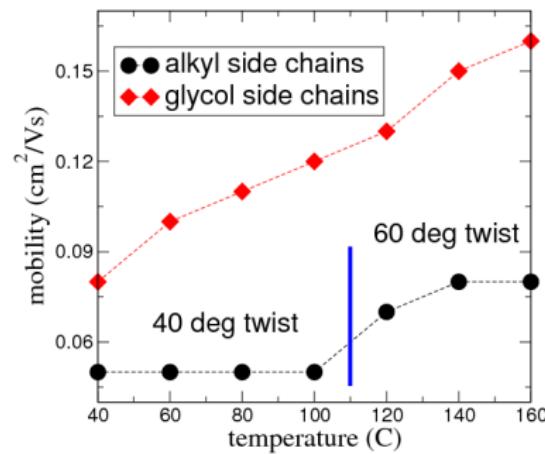
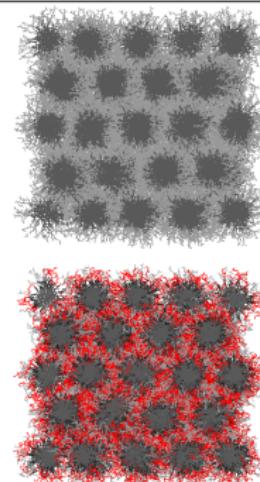
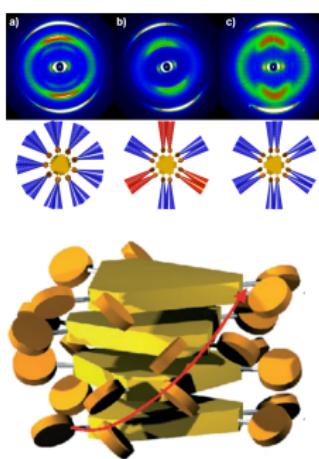
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X. Feng, W. Pisula, V. Marcon, J. Kirkpatrick, K. Kremer, K. Müllen, D. Andrienko (2008)

Triangular-shaped PAH

# Experimental data

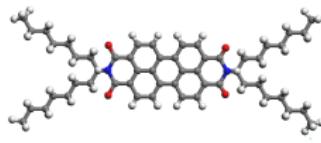
X. Feng, W. Pisula, and K. Müllen - synthesis and characterization  
 V. Marcon, F. Grozema (TU Delft) - mobility measurements



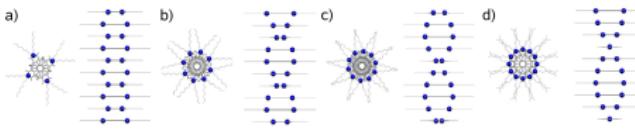
X. Feng, J. Wu, M. Ai, W. Pisula, L. Zhi, J. P. Rabe, and K. Müllen, *Angew. Chem. Int. Ed* 2007

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

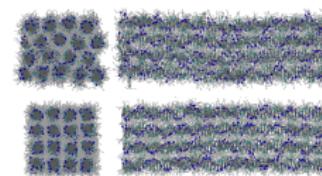
# Perylene diimide



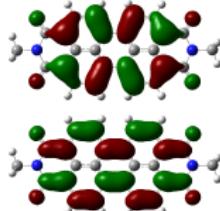
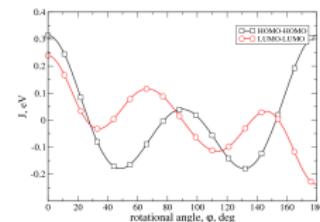
Perylene diimide with branched side chains



Twisted arrangement in columnar phases



MD snapshots

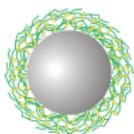
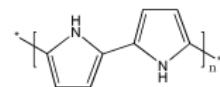


Transfer integral at 3.6 Angstrom

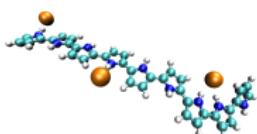
V. Marcon J. Kirkpatrick, W. Pisula, D. Andrienko **Phys. Stat. Solidi B** (2008)

## Conjugated polymers

## Polypyrrole



core-shell architecture for conductive inks



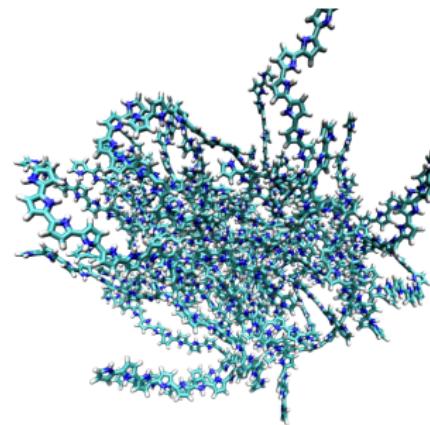
conductive in the oxidized state



ab-initio calculations for charge transport parameters



coarse-graining needed to obtain morphologies

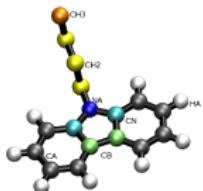


oxidized/reduced polymer morphologies

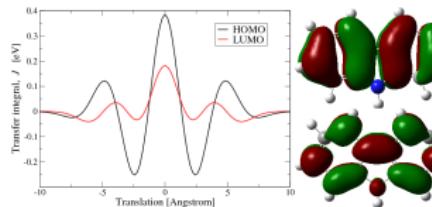
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V. Rühle, J. Kirkpatrick, K. Kremer, D. Andrienko *Pys. Stat. Sol. B* (2008)

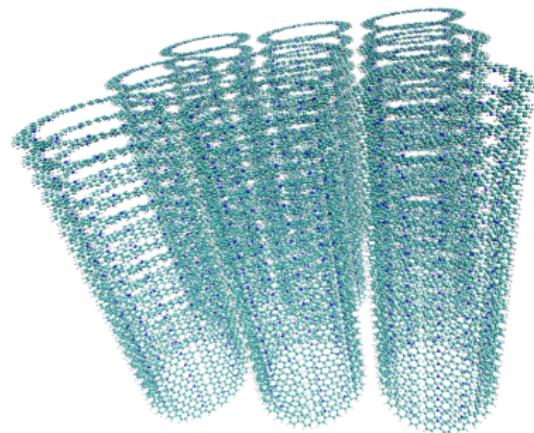
# Carbazole monomers and oligomers



Carbazole repeat unit



Transfer integral at 3.6 Angstrom



MD snapshots

T. Vehoff, J. Kirkpatrick, K. Kremer and D. Andrienko, *Phys. Stat. Sol. B* (2008)

S.-H. Jung, W. Pisula, A. Rouhanipour , H. J. Räder, J. Jacob and K. Müllen, *Angew. Chem.* (2006).

# Collaborations and financial support

- V. Marcon, V. Rühle, T. Vehoff, K. Kremer
- J. Kirkpatrick, J. Nelson (IC London)
- A. von Lilienfeld-Toal (SANDIA)
- W. Pisula (Evonik), X. Feng, K. Müllen (MPIP)
- J. J. Wang, G. Wegner (MPIP)
- C. Jeong, D. Yoon (SNU)
- G. Floudas (University of Ioannina)
- F. Grozema (TU Delft)



Alexander von Humboldt  
Stiftung / Foundation



k€

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- DFG grant "Adaptive multiscale simulation for organic electronics" [V. Rühle]
- Alexander von Humboldt Foundation [V. Marcon]
- MMM initiative of MPG [J. Kirkpatrick]



2007

# Projective method

Our task is to calculate the following integral

$$J = \langle \Psi^A | \mathcal{H} | \Psi^B \rangle$$

$A, B$  denote whether charge is localized on a molecule  $A$  or  $B$ .

Using Slater rules and assuming that  $\Psi_{A,B}$  differ only by the HOMO orbital we obtain

$$J = \langle \phi_{\text{HOMO}}^A | \mathcal{F} | \phi_{\text{HOMO}}^B \rangle$$

A molecule with  $N$  electrons is represented by  $N/2$  molecular orbitals (MOs).

$$\varphi_i^{A,B} = \phi_{ij}^{A,B} \chi_j^{A,B}$$

Correspondingly, the MO of a dimer read

$$\varphi_i^{AB} = \phi_{i,j}^{AB} \begin{pmatrix} \chi_j^A \\ \chi_j^B \end{pmatrix}$$

Projecting  $\varphi_i^{AB}$  on  $\begin{pmatrix} \phi_i^A \\ \phi_i^B \end{pmatrix}$  we obtain

$$\phi^{AB,\text{loc}} = \begin{pmatrix} \phi^A & 0 \\ 0 & \phi^B \end{pmatrix}^T \phi^{AB}$$

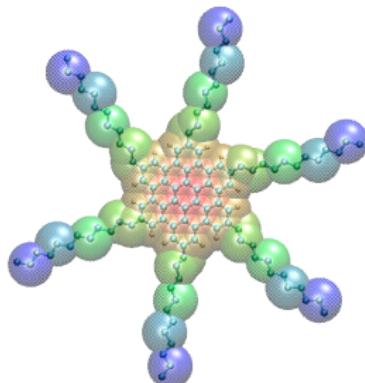
Using eigenvalues of a pair  $\epsilon^{AB}$  we can rewrite the Fock matrix in the localized basis set

$$F^{AB,\text{loc}} = (\phi^{AB,\text{loc}})^T \epsilon^{AB} \phi^{AB,\text{loc}}$$

Now if HOMO is  $i$ th orbital, we would simply read the off-diagonal element  $F_{i,i+N/2}^{AB,\text{loc}}$



# 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.

$$P(\{x_1, x_2, \dots, x_N\}) = \prod_{i=1}^N P(x_i).$$

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

**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)