

# Structure–charge mobility relation for hexabenzocoronene derivatives

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Charge mobilities of several derivatives of discotic liquid crystals have been determined by combining three methods into one scheme: (i) quantum chemical methods for the calculation of molecular electronic structures and reorganization energies (ii) molecular dynamics for simulation of the relative positions and orientations of molecules in a columnar mesophase, and (iii) kinetic Monte Carlo simulations and Master Equation approach to simulate charge transport. Ap-

plying this scheme to differently substituted hexabenzocoronene derivatives we reproduce the trends and magnitudes of mobilities as measured by pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) and connect mobility directly to the microscopic morphology of the columns. Our study also shows that it is possible to understand and reproduce experimental charge transport parameters, and, in some cases, accurately predict them.

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Organic  $\pi$ -conjugated materials have successfully been tested for use in a number of electronic devices, such as field effect transistors, light emitting diodes, and solar cells [1, 2]. However, a detailed understanding of the microscopic origins of underlying physical properties of these materials is still lacking. In particular, the relation of charge carrier mobilities to the material morphology, local molecular ordering, ability to self-assemble, presence of structural defects, etc. is far from being understood.

Among  $\pi$ -conjugated materials discotic thermotropic liquid crystals are unique in a sense that they combine the fluidity of liquids (easy to process, self-healing abilities) with the orientational order of crystals (anisotropic conducting and optical properties [4]). The orientational order arises from the anisotropy of the molecules, in our case a flat aromatic core with aliphatic chains attached at the edges. Typical examples of discotics are shown in Fig. 1. By tuning the shape and size of the conjugated core [5, 6] as well as the type of the attached side chains, compounds with different ability to self-organize and conduct charge carriers can be obtained [7, 8].

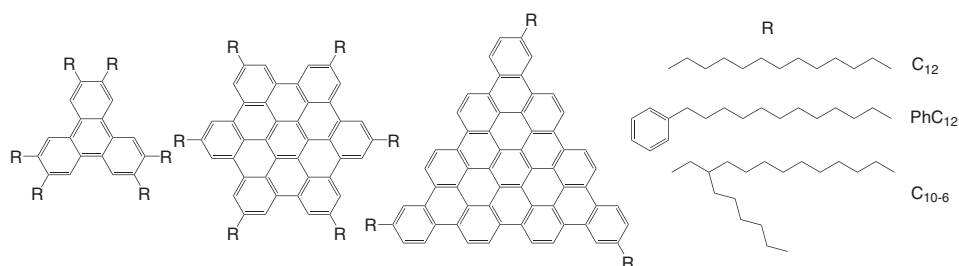
It would of course be helpful to get an insight into the conducting properties of a mesophase prior to the actual

synthesis. A good starting point here is provided by semiclassical electron-transfer theory [9, 10]. This theory predicts that the electron (hole) transfer (hopping) rate  $\omega_{ij}$  from two identical molecules  $i$  and  $j$  in the absence of an external electric field can be written as

$$\omega_{ij} = \frac{|J_{ij}|^2}{\hbar} \sqrt{\frac{\pi}{\lambda kT}} \exp\left[-\frac{\lambda}{4kT}\right], \quad (1)$$

where  $J_{ij}$  is the transfer integral for electron (or hole) transfer,  $\lambda$  is the reorganization energy,  $\hbar$  Planck's constant,  $k$  Boltzmann's constant and  $T$  the temperature.

In spite of strong limitations imposed by the approximations used to derive Eq. (1) (e.g.  $J \ll \lambda$ , single promoting frequency, high temperature limit), it provides two key parameters governing charge transport in disordered materials. The first one, the reorganization energy  $\lambda$ , has two contributions: external, which accounts for any environmental relaxation and changes and internal, which includes only the reorganization energy of the molecules involved in charge transfer. In the case of charge transfer in polar solvents (e.g. in biosystems) the outer sphere component is very large due to the large polarisability of the surrounding; in conjugated polymers and small molecules, po-



**Figure 1** Molecular structures of typical discotics: triphenylene, hexabenzocoronene, and triangular polyaromatic hydrocarbon (PAH) [3]. The side chains can vary from linear alkane chains, such as  $C_n$  with  $n = 10, 12, 14, 16$ , to branched alkane side chains, e.g.  $C_{10-6}$ , to dodecylphenyl-substituted side chains,  $PhC_{12}$ .

larisability is much weaker and internal reorganization dominates. In this case the reorganization energy for the hole transport can be expressed as [11]

$$\lambda = E_+^n - E_0^n + E_0^c - E_+^c, \quad (2)$$

where  $E_0^n$  and  $E_+^c$  represent the energies of the neutral and cation species in their lowest energy geometries, respectively, while  $E_0^c$  and  $E_+^n$  represent the energies of the neutral and cation species with the geometries of the cation and neutral species, respectively (superscript refers to the geometry and subscript to the charge). This description holds as long as the potential energy surfaces are harmonic. Typical values for the internal reorganization energies are given in Table 1.

The second parameter, the transfer integral  $J_{ij}$ , describes the strength of the interaction between two neighboring units. The transfer integral can be computed either by taking a half of the splitting of the HOMO (for holes) or LUMO (for electrons) levels of a dimer [12, 13], by direct evaluation of the orbital overlap [14], or by the projective method [14–16].

For discotics the transfer integral has been shown to be very sensitive to the relative position and orientation of the neighboring molecules [17]. Indeed, in case of the compounds shown in Fig. 1, the molecular alignment most favourable for charge transport is the cofacial one; a 60 deg twist between the neighboring molecules also provides a suitable register for all molecules except of triphenylene. Similar calculations predict that the transfer integral decays exponentially as a function of intermolecular separation; for the three systems shown in Fig. 1 the approximate dependence is  $J \sim \exp(-2.2z/\text{\AA})$ .

Complementing the systems studied in [17], this quantum chemical calculations exemplify how knowledge of the parametric dependence of the transfer integral on relative positions/orientations of two molecules can be very helpful or molecular structure design. It teaches us that, apart from

providing good self-assembling properties, the role of side chains is (i) to minimise the intermolecular distance and (ii) to provide an appropriate azimuthal register for the cores (face-to-face or 60 degtwist). This route for material design is, in fact, being actively followed by synthetic chemists [3, 18–20].

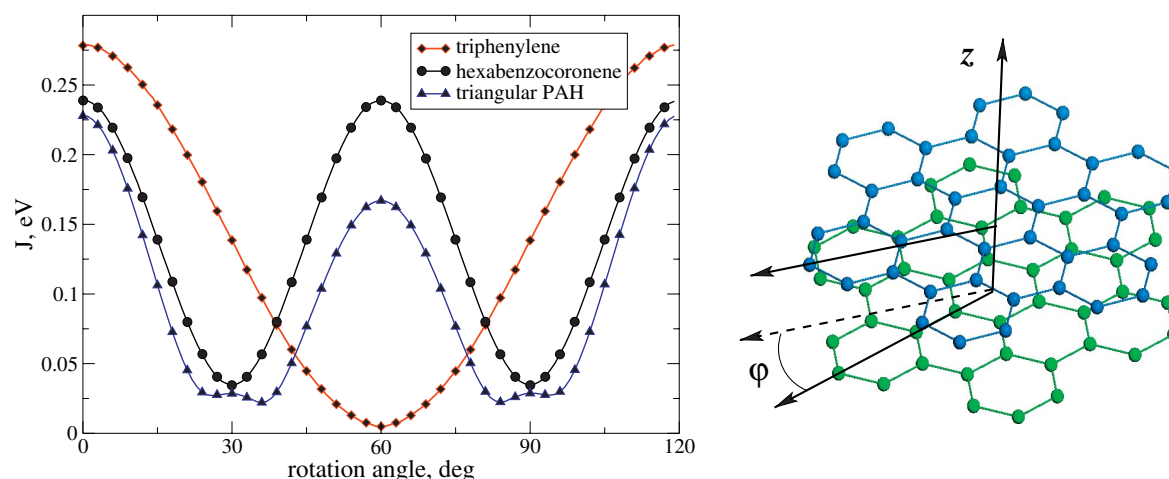
However, knowledge of the parametric dependence of the transfer integral on the relative molecular positions and orientations does not allow to predict the absolute value of charge mobility. To understand why this is the case, let us again have a look at the dependencies shown in Fig. 2. The transfer integral here is very sensitive to the rotational angle; hence, even small variations of relative molecular orientations can lead to significant changes of hopping rates. Discotic liquid crystals, as well as many other organic materials belonging to soft condensed matter, are relatively disordered materials, with a significant entropic contribution to their free energy. Therefore, even in an ideal situation one has a *distribution* of the molecular positions and orientations. In addition, if the intermolecular interaction energies are of the order of  $k_B T$ , these distributions undergo significant thermal fluctuations. It is clear that these distributions, which we further refer to as the morphology of a system, will affect the macroscopic parameters of the mesophase, in particular charge mobility [15, 17, 23].

Hence, for the predictive description of the properties of organic semiconductors, calculations of the transfer integrals shall be complemented by an accurate prediction of material morphology. This, however, is a challenging task, even though a variety of theoretical methods are available. The existing methods can be classified by the length- and time-scales they are employed to study, e.g. phase-field approaches [24], mesoscopic simulations, atomistic molecular dynamics, density functional theory, etc. Not all methods, however, are applicable: the predicted morphology shall be accurate enough for the subsequent calculation of transfer integrals, implying at least atomistic level of description. This eliminates the very coarse methods, such as phase-field approaches. On the other hand, one has to treat rather large systems in order to be able to study defects or include domain boundaries. This is clearly beyond the current abilities of density functional techniques.

The appropriate morphologies, at least on a local scale, can be obtained using molecular dynamics (MD) simula-

**Table 1** 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



**Figure 2** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Evolution of the transfer integral as a function of the rotational angle. The two molecules are parallel to the  $x,y$ -plane.  $\phi$  is the rotational angle around the  $z$ -axis,  $\phi = 0$  corresponds to the cofacial alignment. Geometry optimisation: B3LYP/6-311++g(d,p), molecular orbitals are calculated with ZINDO. Transfer integral is obtained using molecular orbital overlap method [14]. Intermolecular distance is 3.6 Å.

tions. MD is still limited to nanometre lengthscales and a hundreds of nanoseconds timescales. This prohibits studies of large systems as well as molecular self-organisation. The limits of MD can partially be overcome by using coarse-graining techniques, which allow to increase system sizes and simulation time scales by order(s) of magnitude while preserving the atomistic level of description. For details, see the contribution of Rühle et al. in this issue [38].

If an experiment provides sufficient information about the global arrangement of molecules (for columnar mesophases of hexabenzocoronene its crystal structure can be obtained from X-ray [21, 22] and NMR [29]) it is possible to use MD and equilibrate the local structure of the mesophase. In what follows, we illustrate this on discotic mesophases of hexabenzocoronene derivatives with different side chains.

Molecular dynamics relies on the introduction of various atom types and an expression for the potential energy of the system, which is normally given by the following sum of contributions

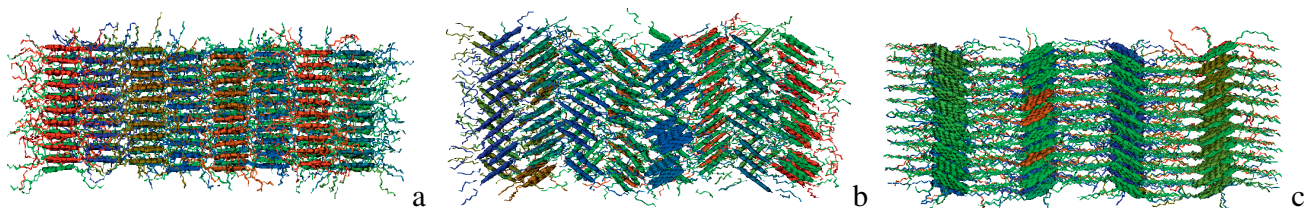
$$E = \sum_{\text{bonds}} \frac{1}{2} K_b (r - r_0)^2 + \sum_{\text{angles}} \frac{1}{2} K_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} \sum_{n=1}^3 \left\{ \frac{V_n}{2} [1 + (-1)^{n+1} \cos n\phi] \right\} + \sum_{\text{impropers}} K_d (\psi - \psi_0)^2 + \sum_i \sum_{j>i} \left\{ \frac{1}{4\pi\epsilon\epsilon_0}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

The first four terms in Eq. (3) correspond to the energy due to the bonded interactions: harmonic bonds (1–2 interactions), angles (1–3 interactions), and torsions, which include proper and improper dihedrals (1–4 interactions). Most of the parameters can be taken from the existing, e.g. AMBER [25] and OPLS [26], force fields, but some of the parameters shall be refined using quantum chemical methods (bonded parameters, e.g. torsion potentials between the aromatic core and the side chains) and experimental data (non-bonded parameters), as discussed in the contributions by Vehoff et al. [39] and Rühle et al. [38]. The parameters of the refined potentials will be published elsewhere.

Once the force field is refined and, most importantly, validated, one can accurately describe the local arrangement of molecules in a mesophase. To do this one still requires the information about the global arrangement of molecules. In case of HBC molecules, experiments (X-ray

and differential scanning calorimetry) suggest that molecules pack in columns arranged on a rectangular (herringbone) or hexagonal lattice [35, 34]. Pre-arranging the molecules on the experimentally predicted lattice one can equilibrate the system locally using standard thermostats/barostats [27].

The results of such an equilibration are shown in Fig. 3. The MD snapshots (a) and (b) are taken at the same temperature, 400 K. The clear difference in packing originates from different side chains: in case of linear side chains,  $C_{12}$ , the packing is almost perfect; the branched side chains,  $C_{10-6}$  lead to a more pronounced local disorder in the system. Hence, one is able to study the effect of the side chain substitution on the local packing of hexabenzocoronene derivatives [27]. The snapshot (c) shows a herringbone packing of the molecules with  $C_{12}$  side chains. Even



**Figure 3** (online colour at: [www.pss-b.com](http://www.pss-b.com)) MD snapshots of columnar mesophases. (a)  $C_{12}$  side chains, 400 K; (b)  $C_{10-6}$  side chains, 400 K; (c)  $C_{12}$  side chains, 300 K (herringbone phase).

though the atomistic MD relies on the global morphology provided by experiments, it can predict some phase transitions. For example, simulated annealing of the herringbone phase leads to a lattice rearrangement into hexagonal columnar packing. The transition temperature predicted by simulation agrees well with experimental data, at around 380 K.

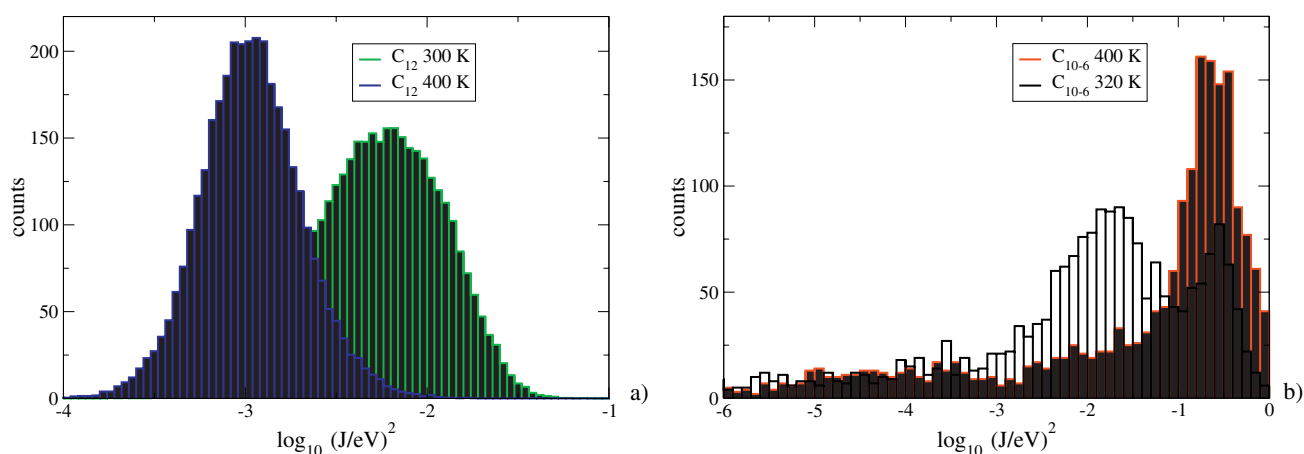
Once the morphologies are known, the overlap integrals  $J_{ij}$  between intercolumnar nearest neighbors  $i$  and  $j$  can be calculated. To do this, the aromatic core of each molecule, as output by the MD simulation, is replaced by a rigid copy of the energy minimised configuration, with the same axial and torsional orientation. The distributions of the transfer integrals,  $\log |J|^2$ , are shown in Fig. 4. It is clear that the mesophase symmetry (which is controlled by temperature) has an immense effect on charge mobility: the herringbone mesophase has higher mobilities, since the average value of transfer integrals for herringbone packing (300 K) is more than one order of magnitude higher than that of hexagonal packing at 400 K. Note that the distributions have practically Gaussian shape, which is assumed a priori in phenomenological descriptions of charge transport [30, 31].

The distributions of more disordered systems, with  $C_{10-6}$  side chains are quantitatively and qualitatively different. First, the transfer integrals are shifted towards higher values, due to better azimuthal register ( $\varphi = 60^\circ$ , see Fig. 2) of molecules. Second, at low temperatures (herringbone mesophase, 320 K) the distribution is double-peaked, due

to formation of well aligned domains of molecules with slightly different distances between the molecules at the domain boundaries (a typical size of a domain is 5–6 molecules). Finally, there is a long tail extending to the side of small  $J^2$ . This tail lowers the mobility, since in one-dimensional transport the mobility is limited by the slowest rates. It is clear that these distributions cannot be approximated with a single Gaussian.

Once the hopping rates  $\omega_{ij}$  are known, one can map MD snapshots on a lattice where each lattice point is the centre of mass of a molecule and the hopping rates are given by Marcus' Eq. (1). The charge dynamics can then be computed either using the master equation approach or kinetic Monte Carlo. The details of such calculations for a series of HBC derivatives are presented in Ref. [28], and show excellent agreement with PR-TRMC experiments [32, 33]. Of course, a direct comparison with time-of-flight measurements [36] is not possible, since we treat only small, well-ordered domains, as does PR-TRMC. One can overcome this limitation by using coarse-graining techniques to simulate the large-scale morphologies [37].

To conclude, the combination of quantum chemical methods for calculation of molecular electronic structures and reorganisation energies, combined with molecular dynamics simulations of morphologies and kinetic Monte Carlo methods to simulate charge dynamics, allows one to understand the microscopic origins of charge transport and



**Figure 4** (online colour at: [www.pss-b.com](http://www.pss-b.com)) 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 (320 K) and hexagonal (400 K) of HBC with dove-tail side chains.



predict charge mobilities on a local scale. The technique described above is also extendable to other systems, as well as to other problems: MD simulations are capable of predicting mesophase transitions, e.g. from a herringbone to a hexagonal columnar arrangement. Analysis of molecular packing in two mesophases allows to explain why, for example, charge mobility is about two times higher in a herringbone mesophase than in a hexagonal one. An overview of the temperature dependence as well as the effect of phase transitions on charge mobility is given in the contribution by Kirkpatrick et al. [40]. Another example, a study of charge transport in helical columnar mesophases of perylene diimide derivatives is reported in a contribution by Marcon et al. [41].

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