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Structure and Dynamics of a Model Discotic Organic Conducting Material

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Abstract. Organic conducting materials exhibit promising functionalities, inducing hence a keen interest due to their potential use as a next generation photoconverters. However, unlike the more expensive inorganic analogues, the underlying properties that give rise to these advantages also cause organic materials to be inherently inefficient as photovoltaics. Understanding their properties at the microscopic level is a major step towards an efficient and targeted design. We probed the morphological and dynamical aspects of a model organic discotic liquid crystal material hexakis(n-hexyloxy)triphenylene (HAT₆) by using neutron-based diffraction and quasielastic scattering techniques to gain deeper insights into structure and dynamics. The neutron measurements are accompanied, in a synergistic way, by molecular dynamics simulations for the sake of the analysis and interpretation of the observations.

1. Introduction

Due to their potential applications as photovoltaic energy-converters and thanks to their low cost, inherent flexibility and relative ease of processing, organic conducting materials offer a better alternative to the traditional, cost-prohibitive, inorganic semiconductors [1, 2, 3]. When disc-shaped poly-aromatic molecules are decorated with aliphatic side chains, they may self-assemble into columnar superstructures with both solid and liquid-like properties [4] arising from the cores and tails, respectively. This leads to properties like self-healing of defects and tunable alignment of the conducting columns [5]. In this context, discotic liquid crystals (DLCs) are a promising class of materials for molecular electronic devices, such as light emitting diodes, field-effect transistors and solar cells. These disk-like molecules with poly-aromatic cores stack on top of one another to form stable columns, providing one-dimensional molecular wires for charge-carrier transport, via a π - π overlap.

The main factor which affects the columnar charge migration in DLCs is the dynamics of the system. That is any conformational change and/or disorder/fluctuations could hinder the π -overlap. Therefore, for a widespread application, the conductivity properties of discotics require optimisation. Indeed, charge transport in these systems requires adequate intermolecular π -orbital overlap of the poly-aromatic cores along the entire columnar wire. The overall conductivity is therefore strongly dependent on the local conformation of the molecules, the presence of structural defects and thermal motions induced by the fluidic side chains [6, 7, 8]. Knowledge of how each of these three factors limits the hopping of charge carriers is valuable



for rational design of discotic compounds with optimal device performance.

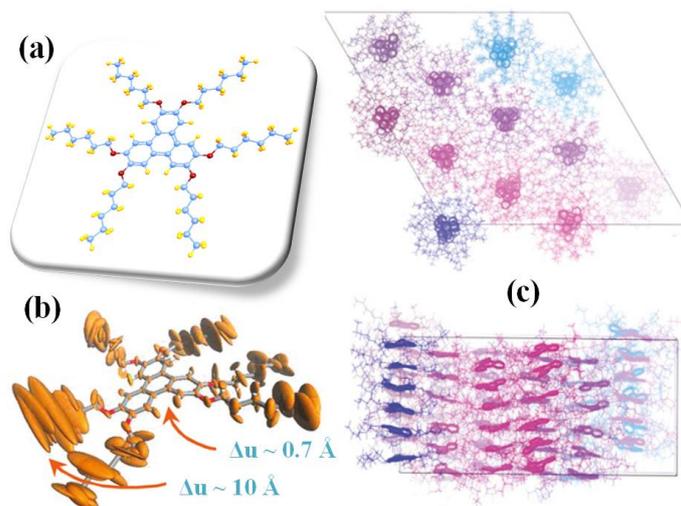


Figure 1. (a) HAT₆ in its starting D_{3h} configuration, (b) anisotropic displacements for a HAT₆ molecule ranging from 0.7 Å (aromatic core) to 10 Å (tail end), and (c) snapshot of a model MD simulation (further details on simulation and structure are provided in Section 2). The colours illustrate the orientational order of the columns. The deviation from the initial D_{3h} symmetry is due to the thermally-activated inter and intra molecular motions. This is pictured in terms of fluctuations and deformations occurring between and within the cores, respectively. The geometrical fluctuations reproduced by MD simulations are consistent with the behaviour of the liquid-crystalline phase.

We have studied various aspects (morphological/structural, dynamical, and electronic) of a model organic discotic liquid crystal material consisting of the molecular system hexakis(*n*-hexyloxy)triphenylene (HAT₆) [8, 9, 10, 11, 12, 13, 14]. In this context, neutron scattering measurements were performed, in the electronic ground state, to gain a deeper and better understanding of the structural and dynamical properties of this material. The neutron measurements were accompanied by Raman and nuclear magnetic resonance probes. At the vibronic level, the low-lying excited states were explored using resonant Raman and UV-vis spectroscopies. Atomistic simulations, either classical via empirical force fields, or first-principles-based via improved density functional theory methods, were used synergistically for the sake of the analysis, interpretation and predictions. However, the presentation here is limited to the application of neutron scattering to probe structure and dynamics of HAT₆. The reader can refer to the indicated literature (and the related references therein) for a complete overview on the other above cited experimental and modelling techniques we have employed to treat this topic.

Neutron scattering is a convenient tool to study the dynamical structure of these systems. Neutron diffraction on deuterated samples generally achieves complementary information to X-ray diffraction. Considering the dynamics, quasi-elastic neutron scattering (QENS) is well suited to probe the picosecond timescale molecular motions of the discoids [15]. We have successfully elucidated the fundamental mechanisms that limit charge transport in discotics, by linking neutron diffraction and QENS experiments directly with classical molecular-dynamics simulation (MD). This enabled us to reveal the dynamic morphology of HAT₆ by determining the effect of dynamical disorder on conductivity [8, 9, 10].

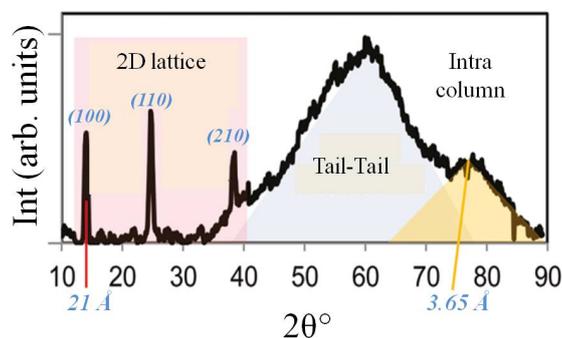


Figure 2. Diffraction pattern of HAT₆ in the columnar phase from neutron measurements. The two-dimensional lattice of columns, and tail-tail and intra-column distances distributions are highlighted.

2. Results and Discussion

HAT₆ (Figure 1(a)) is one of the most basic compounds forming a discotic liquid crystalline phase [7, 16, 17, 18]. The MD simulations were performed on different initial model structures, which were built from a hexagonal superlattice of 12 columns each consisting of six molecules (Figure 1(c)). The initial lattice parameters were determined from the observed reflections in the neutron powder-diffraction pattern (Figure 2), and the measured density of HAT₆. Three regions are distinguishable in the neutron diffraction pattern of a DLC in the columnar phase (Figure 2): (i) a region with three sharp peaks originating from the two-dimensional hexagonal lattice, (ii) the broad distribution of the tail-tail distances form an intermediate region originating, and (iii) a region indicating the intra-columnar distances.

During the MD pre-relaxation of the model structures, the evolution of the simulated diffraction pattern was followed and compared with the experimental data (Figure 3). The crystal structure predicted by the MD simulations reproduces the three regions in the diffraction pattern [9, 10]. The dynamical behaviour of the liquid-crystalline phase is included in the comparison of the MD simulations with the experimental observations. The dynamic behaviour was included by calculating the anisotropic displacements (Figure 1(b)).

We found that different initial models converged towards a comparable overall minimum in configuration space, and consistently resulted in a satisfactory agreement with the experimental diffraction pattern. After the long pre-relaxation run a second MD simulation was performed on the fully relaxed structural models. The diffraction patterns retained their good agreement with experiment during this time evolution, and thermally-averaged structure parameters were obtained (Figure 1(c)).

The experimentally-observed diffraction pattern is intermediate between the simulated patterns of the models. The simulated diffraction pattern of the models TWIST60 and TWIST25 show an excellent agreement with diffraction data. The relaxed structures stem from different starting configurations (the caption of Figure 3 include details of the models). Based on the agreement with the measured diffraction pattern [9, 10], both models converge to comparable minima in configuration space. This happens close to the actual liquid-crystalline structure. Rather than a uniform shift of the core-core distance distribution to higher distances, a high disorder in the core-core distances is actually induced by the competition between the mutual van der Waals

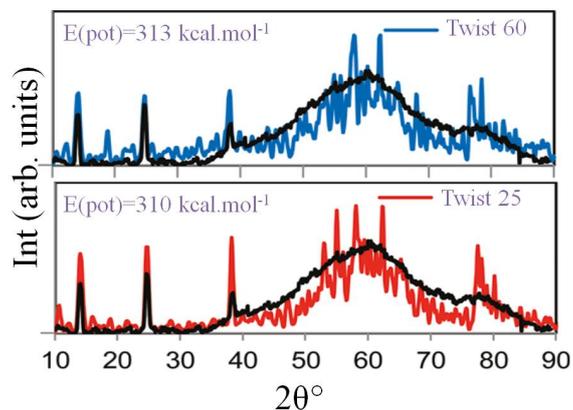


Figure 3. The experimental (black line) and simulated (models TWIST60 and TWIST25) diffraction patterns. The model TWIST60 consists of the rotation of the nearest neighbour molecules in a column by 60° around their principal axis, while a similar orientation is kept for molecules in a two-dimensional layer. On the other hand, the model TWIST25 consists of a unit of three columns built by considering a twist angle of 25° for the first column, then the same mutual rotation angle is applied for the second column, but in the opposite direction. This constrains the twist angle of the third column to 5° , helping hence to avoid superposition of the tails.

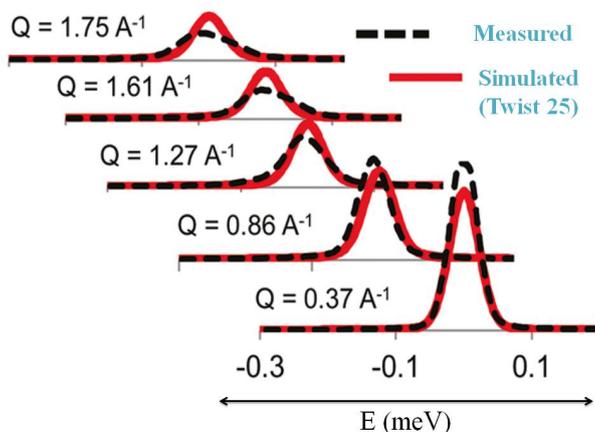


Figure 4. The Q -dependence of the incoherent scattering function from quasielastic neutron scattering measurements (QENS) and molecular dynamics simulations (MD).

interactions of the cores and the steric repulsion of the tails. Indeed, the tails tend to orient toward the open spaces left by these core-core defects. This is supported by the fact that the whole-molecule peak lies at a higher distance in comparison to the core-core peak. The inferred twist-angle distribution values are found to be around 36° . This is close to the DFT-estimated minimum-energy twist angle of 30° [8].

Dynamics occurring on the picosecond timescale can be determined by studying the incoherent-scattering functions which are extracted from MD simulation of the two MD models TWIST25 and TWIST60, and compared directly, for the sake of the validation [9], with QENS experiments

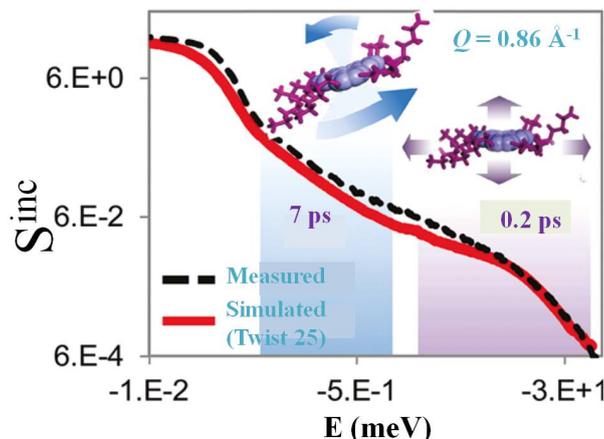


Figure 5. A log scale representation of the simulated and measured incoherent scattering function. The regions of dominant rotational (7ps) and translational (0.2 ps) motions are highlighted.

(Figure 4). The QENS technique offers the opportunity to follow both the temporal and spatial characteristics of the atomic motions, thanks to a well-characterized interaction of the neutrons with the atomic nuclei. Therefore, it is fairly straightforward to estimate the expected spectral profiles by using the atomic trajectories from the MD simulations to assign the time scales of motions to the underlying mechanisms.

The analysis of the experimental data showed that at least two Lorentzian functions (in addition to the elastic peak) are required to perform the fit [9, 15]. Two characteristic timescales of about 0.2 and 7 ps were extracted from the peak widths. Simulations based on these MD models agree well with the measured temporal and spatial dynamics (Figure 5). A closer investigation of the simulation trajectories allowed to characterize the underlying thermal motions, and therefore the typical amplitudes of molecular motions on the 0.2 and 7 ps can be estimated.

The characteristic translational and tilt motions for a single molecule on the 0.2 ps timescale are illustrated in Figure 6. On this timescale the twist-angle deviations are negligible (amplitudes smaller than 0.1°). The tilt degree of freedom of the molecular core seems to be too fast to be followed by the aliphatic tails. The rotational motions are much more pronounced on the 7 ps timescale where the motion of the aliphatic tails is induced by the rotations of the core.

3. Conclusions

We found that molecular translations (in-plane motions) are the dominant contribution to the spectral component of 0.2 ps in the QENS spectrum, whilst the 7 ps component mainly stems from both tilt and twist motions of the whole molecule. In order to determine the effect of local conformation, structural defects and thermal motions on charge transport, the situation for HAT₆ was compared with that of larger discotic molecules exhibiting higher conductivities. It turns out that the large disorder in core-core distances is the major factor limiting the conductivity of HAT₆. The charge hopping rate decreases exponentially as a function of core-core separations. As a result, we consistently found that the structural defects in core-core distances account for a decrease in the mobility by a factor of about 100 in going from larger discotics to HAT₆. The combination of MD simulations with neutron scattering is clearly of a key value for the study of liquid-crystalline phases.

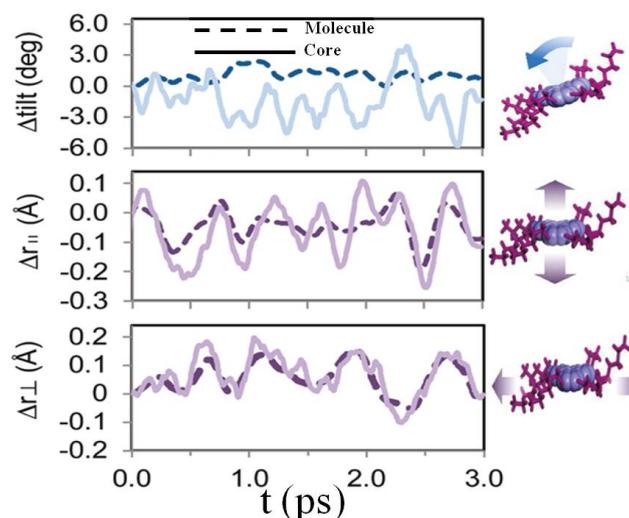


Figure 6. Translational and tilting motions on the sub-picosecond time scale for a typical molecule extracted from the simulated MD trajectory. Both dynamics of the molecular centre of mass (CM) including the tails (dashed lines), and the aromatic core CM alone (solid lines), are shown.

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