Electron Diffraction Studies of Molecular Disorder in TIPS-Pentacene

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Thin film transistors are an application of organic semiconductors that promise large area, low-cost, flexible and cheap alternatives to traditional inorganic semiconductors. The transport properties of these materials are controlled by the spatial arrangement of molecules within the structure that contain conjugated π-electron densities [1]. While the 'bulk' crystal structure of the organic semiconductor TIPS-pentacene [2] has been determined using X-ray diffraction (shown in Figure 1a), the dynamics of the structure, including the movement of the transport-mediating conjugated species, requires a technique displaying greater sensitivity to small atomic displacements and especially one that can readily detect light atoms such as carbon. Electron diffraction is ideal because the strong electron-sample interaction makes it sensitive to both light atoms and small distortions, but also the small beam size available allows analysis from small single grains within a polycrystalline thin film.

CBED patterns from a single grain of a TIPS-pentacene film were recorded at 100K using a Philips CM30 TEM operating at 300kV with a liquid nitrogen stage. Figure 1b shows a pattern recorded parallel to the [001] zone-axis of the crystal (after background correction to highlight the scattering to higher spatial frequencies). The diffuse stripes in the [001] pattern, seen parallel to [120]*, were attributed to disorder in planes with a component parallel to the (120) planes. The lack of diffuse scattering in the central systematic row indicates the disorder has a strongly transverse displacement character. The pentacene molecules lie almost exactly parallel to the (123) planes and with their long axis parallel to the $[2\bar{1}0]$ direction so the origin of the diffuse scattering was determined to be caused by an oscillation of the pentacene molecules within the (123) planes, parallel to their long axis.

Simulations of these oscillations were undertaken using an adapted multislice calculation [3] incorporating the frozen phonon approach, in which an 18x18 supercell of TIPS-pentacene structure was generated and the pentacene molecules could be moved independently. In order to perform such large array simulations (~15000 atoms per slice) a GPU-based multislice program was developed. The molecular distortions were defined by a Gaussian distribution about the equilibrium position along the pentacene long axis. Refinement of the FWHM of the Gaussian led to simulated diffraction patterns (shown in Figure 2a) that match the experimental pattern extremely well.

In order to compare this behaviour with existing models for TIPS-pentacene transport, the existing molecular dynamics simulations for the molecule were used to provide an additional set of atomic positions for the structure. Snapshots of the molecular trajectory were introduced into the multislice calculation and used to generate diffraction patterns for the material under vibration. The simulated diffraction pattern, shown in Figure 2b, is in good agreement with both the experimental pattern and that recovered from the simple phonon model described earlier, suggesting that the pentacene phonon is an accurate description of the dominant feature of the molecular dynamics. The standard deviation of the pentacene position about its ideal was extracted from the molecular dynamics trajectory and found to be 0.084Å, which agreed well with the refined standard deviation of the earlier simulation of 0.07Å.

This data suggests that electron diffraction can be an extremely powerful tool to analyse in a quantitative fashion the dynamic disorder present not only in organic semiconductors, but a wide

range of disordered materials. The development of new approaches to simulate extremely large supercells is essential for accurate quantitative analysis of diffuse scattering [4].

References

[1] D Cheung and A Troisi, Phys Chem Chem Phys, **10** (2008) p.5941
[2] J Anthony *et al*, JACS, **123**, (2001) p. 9482
[3] E Kirkland, Advanced Computing in Electron Microscopy, Plenum Press, New York (1998)
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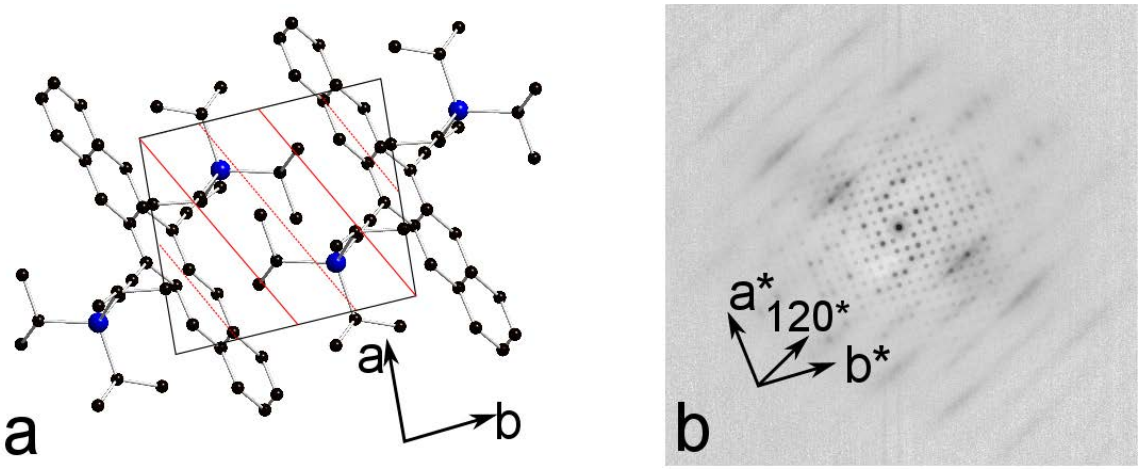

Figure 1. *a) Partial structure of TIPS-pentacene crystal viewed parallel to [001], the (120) and (240) planes are indicated to highlight their relevance to the arrangement of pentacene molecules in the structure. b) experimental diffraction pattern recorded parallel to the [001] zone axis. Background correction has been performed to highlight the diffuse streaks present in the pattern.*

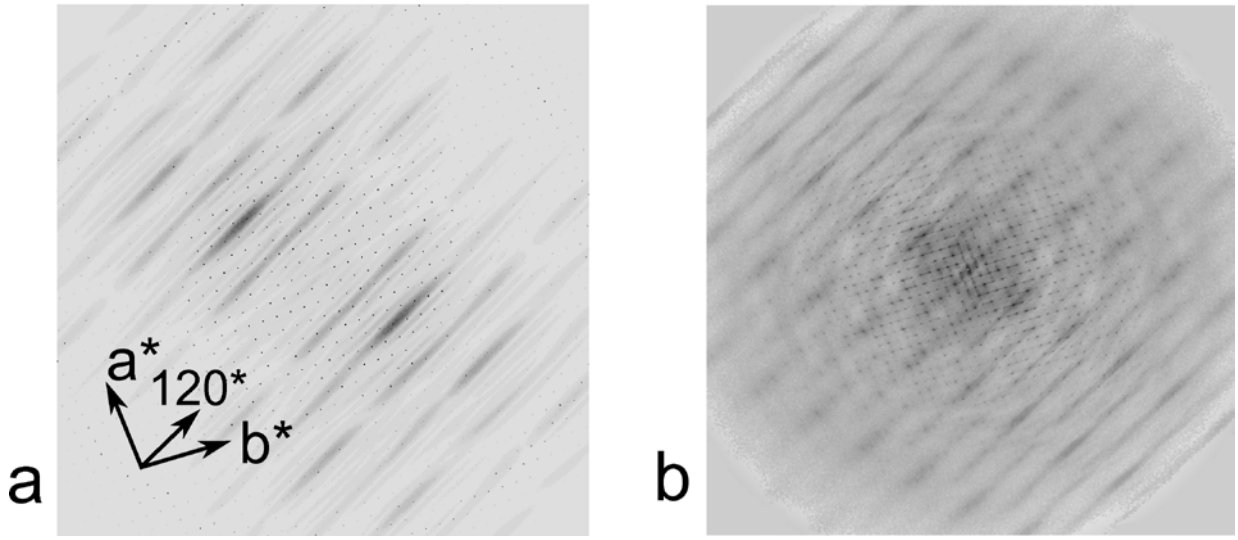

Figure 2. *Simulated [001] zone-axis electron diffraction patterns for TIPS-pentacene, atomic positions were generated from a) a pentacene phonon model and b) molecular dynamics simulations.*