

## Guest molecule diffusion and conformation influenced by local liquid crystal structure

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Optical single molecule investigations are superior to ensemble methods in revealing local structure and dynamics of thin soft matter films. Here we use tailored perylene diimide (PDI) molecules to probe the diffusion of guest molecules in 50 to 200 nm thick films of the liquid crystal 4-n-octyl-4'-cyanobiphenyl (8CB) on silicon with either thin native or 100 nm thick thermal oxide. These PDI molecules are shown to orient with the local liquid crystal director and thus follow the liquid crystal structure [1, 2].

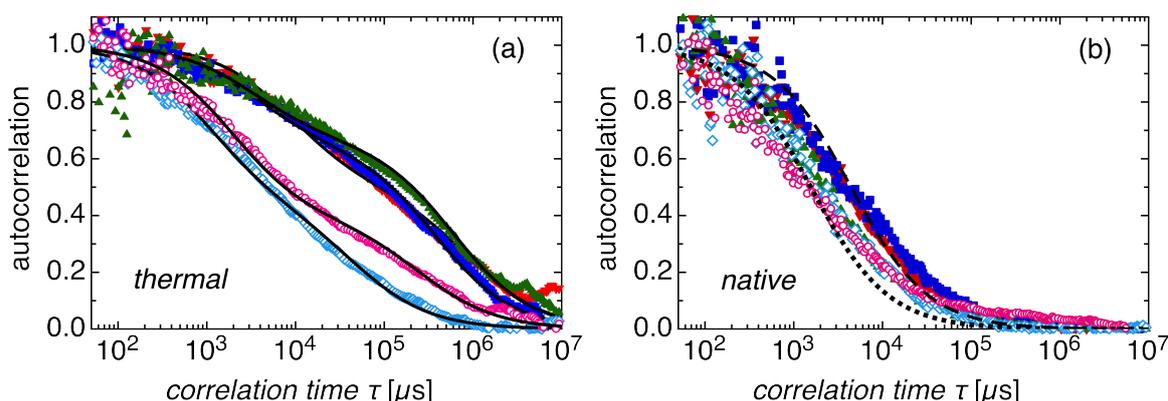


Figure 1: Normalized FCS curves of PDI in 200 nm thick 8CB films on (a) 100 nm thermal and (b) native oxide at (▲) 23°C, (■) 25°C, (▼) 28°C, (◇) 31°C, and (○) 34°C with (a, solid line) two component fits, and (b) one component fit (dashed) for 25°C and (dotted) for 34°C.

Figure 1 shows normalized FCS curves obtained from PDI in 200 nm thick 8CB films at the smectic-nematic phase transition (the bulk transition temperature  $T_{SN} = 33.5^\circ\text{C}$ ). For the film on thermal oxide (a), the correlation curves contain more than one component of diffusion. Fitting improves, when a two component function for lateral diffusion is used (solid lines). Thereby the slow component combines slowed guest molecule diffusion in the interface region with ad-/desorption events. For 31°C (◇) both components are about one order of magnitude faster in respect to the lower temperatures (filled symbols). At about bulk  $T_{SN}$ , at 34°C the obtained FCS curves vary for different positions on the sample (not shown) and tend to yield slower diffusion again (○). The latter can be ascribed to formation of LC domains with different structures [2].

The FCS curves obtained from the 200 nm 8CB film on native oxide do not show the slow component of diffusion from the interface region. In this case, fluorescence correlations spectroscopy (FCS) yields only information about the upper film region, exceeding  $\approx 30$  nm distance to the substrate, because of non-radiative de-excitation of PDI in proximity to the substrate. Nevertheless, also for native oxide, the FCS curves show deviations from fits with single component correlation functions for 2-dimensional diffusion (see dashed line for 25°C). The deviations increase with increasing temperature (see dotted

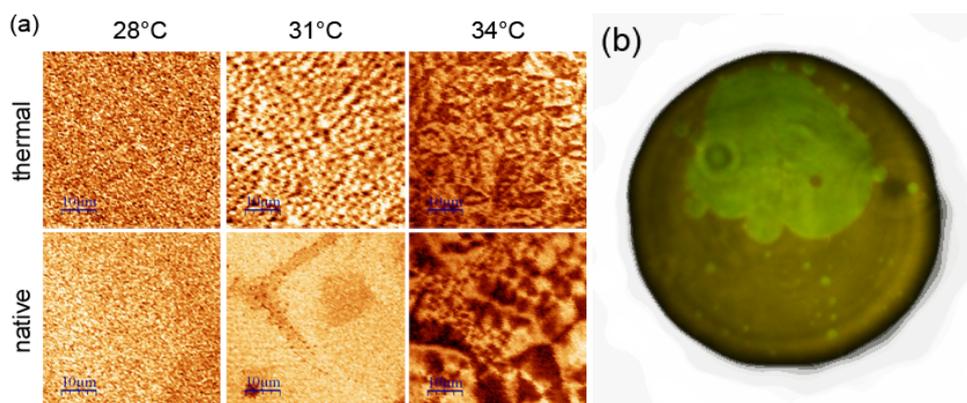


Figure 2: (a) 200 nm thick 8CB films on (top) 100 nm thermal and (bottom) native oxide at the smectic-nematic phase transition shown in reflected light. (b) Fluorescence image of MEH-PPV embedded in 8CB showing regions with different emission spectra.

line for 34°C). This can be ascribed to increasing vertical diffusion causing additional fluorescence fluctuations, which modulate the correlation function.

Thin 8CB films are known to show structure undulations at the nematic-isotropic phase transition [3] and so called focal conic domains in the smectic A phase when cooled from the nematic phase [2]. Figure 2a shows images in reflected light from 200 nm thick 8CB films on (top) 100 nm thermal and (bottom) 2 nm native oxide at 28°C, 31°C, and 34°C. During this approach of the smectic to nematic phase transition, the film on thermal oxide shows small sized structures already at 31°C (middle). At this temperature, larger sized structures start to appear on native oxide. At 34°C (right) the film on native oxide still shows larger sized and less regular structures compared to the film on thermal oxide, which can be interpreted as slower phase transition dynamics on native oxide. This points to an influence of long range van der Waals interaction on self-diffusion [4]. Further information on local dynamics is expected from extended FCS studies during phase transition.

Due to their relevance for technical applications, conjugated polymers are promising materials for further guest molecule studies. Preliminary investigations show an influence of the liquid crystal structure on the emission spectra and thus the conformational order [5] of the conjugated polymer poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene) (MEH-PPV) embedded in 8CB, see Figure 2b.

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## References

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