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Title: Synthesis and characterization of novel azobenzene-based mesogens and their organization at the

air-water and air-solid interfaces

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Abstract:

Eight new oligomeric mesogens are reported, consisting of an azobenzene-based core attached to which are four 4-cyanobiphenyl units via flexible alkyl spacers (n = 5-12). Their chemical structures were determined by 1H NMR, 13C NMR, IR, UV-Vis and Raman spectroscopy, and elemental analysis. The thermotropic liquid crystalline properties of these materials were investigated by POM, DSC and XRD. The oligomers containing n = 8 and n = 10 were found to exhibit a monotropic nematic (N) phase while others were non-mesomorphic. Langmuir monolayers and Langmuir-Blodgett films of the nematic compounds (n = 10) were studied at the air-water interface (Langmuir film) and the air-solid interface. Surface manometry studies on the Langmuir monolayer showed that the film had nearly zero surface pressure at a large area per molecule (Am ≥ 0.55 nm2). The film on compression showed a gradual increase in surface pressure and finally collapsed at an Am of about 0.15 nm2 with a collapse pressure of about 60 mN m-1. Brewster angle microscopy (BAM) images (during compression) showed that dark regions coexisting with grey spots in large areas transformed to a uniform grey region with an increase in surface density and finally collapsed exhibiting bright regions. Atomic force microscopy studies (AFM) on the LB films, transferred onto freshly cleaved hydrophilic mica substrates, exhibited a network of thin fibers with the height of fibers varying between  $\sim$ 4 nm to 80 nm which could be due to  $\pi$ – $\pi$  stacking and dipolar interactions associated with the cyanobiphenyl units. On a hydrophobic silicon substrate, the LB transfer yielded a multilayer film which dewetted to form nanodroplets. We carried out temperature dependent AFM studies of the nematic compounds which showed the reversible formation of aligned fibers (~20 to 40 um) in the mesophase. In brief, our study provides new approaches for the realization of controlling the anisotropic properties of an ordered phase.

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