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Confinement effects and multiple glassy dynamics for a homologous series of triphenylene-based columnar liquid crystals – A study by broadband dielectric spectroscopy, advanced calorimetry and neutron scattering

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Hexakis(n-alkyloxy)triphenylene) (HATn) consisting of an aromatic triphenylene core and alkyl side chains are model discotic liquid crystal (DLC) systems forming a columnar mesophase. In the mesophase, the molecules of HATn self-assemble in columns, which has one-dimensional high charge carrier mobility along the columns. Here, a homologous series of HATn with different length of the alkyl chain (n=5,6,8,10,12) is investigated using differential scanning calorimetry (DSC), broadband dielectric spectroscopy (BDS) and advanced calorimetric techniques including fast scanning calorimetry (FSC) and specific heat spectroscopy (SHS). The investigation of the phase behavior was done utilizing DSC experiments and the influence of the alkyl chain length on the phase behavior was revealed. By the dielectric investigations a γ-relaxation due to localized fluctuations as well as two glassy dynamics the αcore and αalkyl relaxation were observed in the temperature range of the plastic crystalline phase. Moreover, the observed glassy dynamics were further studied employing advanced calorimetry. All observed relaxation processes are attributed to the possible specific molecular fluctuations and discussed in detail. From the results a transition at around n=8 from a rigid constrained (n=5,6) to a softer system (n=10,12) on a molecular lenght scale was revealed with increasing alkyl chain length. A counterbalance of two competing effects of a polyethylene like behavior of the alkyl chains in the intercolumnar domains and self-organized confinement is discussed in the context of a hindered glass transition. The results were confirmed by in- and quasielastic neutron scattering.

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