Discotic liquid crystals (DLCs) are materials where self-assembly is driven by non-covalent intermolecular interactions. During the self-organization process, the disk-shaped molecules organize into columns that further assemble into two-dimensional arrays whereas the alkylic chains fill the intercolumnar space. Highly ordered columnar structures of hexa-peri-hexabenzocoronenes (HBC) were found to be very promising as active semiconductors in organic FETs (molecular wires) and photovoltaic devices. The self-assembly and molecular dynamics in a series of dipole functionalized nanographenes were studied using thermodynamic (DSC, PVT), structural (WAXS) and dynamic (DS, site-specific NMR, Rheology) probes [1-5]. These DLCs undergo a phase transformation from a dipolar ordered but structurally disordered liquid crystalline (LC) phase at higher temperatures to a dipolar disordered but structurally ordered crystalline phase (Cr) at lower temperatures [4]. The effect of dipole substitution is to change the energetics and to stabilize the LC phase. Within the LC phase the intra- and inter-columnar thermal expansions were different but both positive. In contrast, the Cr phase shows a negative thermal expansion (NTE) [3]. With respect to the dynamics, these small molecules display a range of hierarchical molecular motions (i.e. polymer-like) ranging from 0.01 ps to hours as shown by FTIR, NMR, DS and Rheology [5].