In general, the pursuit for highly efficient electronic organic materials is limited by the molecular mobility and its control. For instance, to achieve a large electro-optical activity in non-linear dipole chromophore systems, one needs to control their susceptibility to undesired aggregation during the forced aligning process (poling) of the chromophores. With the growing complexity of the molecular building blocks of electronic organic materials, and the decreasing system sizes (e.g., ultrathin films) the characterization tools have to evolve. In this paper, we present a nano-rheological technique based on scanning force microscopy that offers a quantitative approach for investigating the mobility/stability of organic semiconductors ultrathin films. Local properties such as energy barriers for sub-molecular motions (relaxations) and critical transition temperatures can be measured directly on films on relevant substrates (e.g., ITO glass) that are later used in actual devices. Recent results related to photonics and optoelectronics are discussed, such as the improvement of the optical efficiency and the enhancement of the spectral stability.