In recent years we observe rapid development of miniaturized electronic devices, which directs research attention toward synthesis of new functional materials. Among many different approaches the one based on utilization of organic semiconductors attracts growing attention and is a subject of broad studies. One of the most often studied single molecule organic semiconductor is pentacene – the longest acene stable in ambient conditions. Acenes are promising organic molecules containing linearly fused benzene rings. Theoretical studies predict that longer acenes should exhibit even more outstanding properties being ideal candidates for applications in organic light emitting diodes, organic field effect transistors and other photovoltaic devices. It is expected that with increased number of fused rings acenes would be characterized by smaller HOMO-LUMO gap, weaker electron-phonon coupling and lower reorganization energies. Moreover it is envisioned that sufficiently long acenes should exhibit interesting magnetic properties, which make them promising candidates for applications in new areas, e.g. spintronics. However, although higher acenes are predicted to posses interesting properties, their synthesis and characterization is still a challenging task, due to their intrinsic instability and reactivity, which grows when new rings are annealed. In effect in recent years several new stabilization strategies have been introduced to overcome problems and synthesize some higher acenes and their stabilized derivatives. However, it was only recently when the approach based on surface-assisted chemistry applied in ultrahigh vacuum conditions allowed for synthesis and electronic characterization of higher parent acenes. In general, in recent 15 years the on-suface synthesis has proven to be a powerful tool for generation of intrinsically instable molecules and their subsequent detailed characterization. Moreover, the enormous progress in the development of scanning probe techniques allowed achievement of unprecedented resolution in organic molecule visualization based on non-contact atomic force microscopy with functionalized tips. Furthermore electronic properties of synthesized molecules could be spatially mapped using scanning tunneling microscopy and spectroscopy measurements. This project will be aimed at the generation, detailed structural and electronic characterization of higher acenes and their derivatives on metallic substrates. In particular we will investigate the possibility to increase molecule stability by structural modifications focused on preserving acene outstanding intrinsic electronic properties. Furthermore we will face the challenging task aimed at on-surface fabrication of more extended and sophisticated covalently bonded acene-based molecular architectures and their functionalized derivatives. As a result of our research the new strategies toward synthesis of molecular nanostructures with tailored electronic properties will be analyzed and described providing novel organic semiconductors. Their structural and electronic properties will be thoroughly in-detail characterized based on scanning probe measurements.