The use of organic semiconductors provides inexpensive and simpler production of electronics. We thus want to pursue examining the electronic properties of organic semiconductors. In particular, we examined pentacene and rubrene. In analyzing each we used reflection high energy electron diffraction (RHEED) and angle resolved photoemission spectroscopy (ARPES). Our samples were prepared on a Bi:Si(111)-7×7 surface using molecular beam epitaxy. RHEED was used to confirm that our surfaces were smooth and of a single crystal; however, we were not able to achieve a rubrene film despite trying bismuth and pentacene substrates as well as various growth parameters. In contrast to rubrene, pentacene did grow epitaxially on bismuth, and RHEED was also used to determine the lattice constants of our pentacene samples, which we found to match the polymorph 6.0Å × 7.9Å × 86°. ARPES was performed on rubrene samples. The highest occupied molecular orbital (HOMO) peak was seen in our Rn:Bi:Si sample, but it was not single-crystal as shown by RHEED. The HOMO peak was not detected in the Rn:Pn:Bi:Si sample when the rubrene was grown on a warm (80°C) pentacene substrate; however, the rubrene HOMO peak was seen when the pentacene substrate was at room temperature. Our ARPES data of the rubrene HOMO peak gives evidence to hole/vibration coupling.