Oriented thin films of organic semiconducting small molecules have received considerable attention as active semiconductors for device applications such as Schottky diodes and thin-film transistors (TFTs). Among these organic materials, pentacene has been found to have the highest mobilities for hole transport. Understanding the formation of self-organized ad-layers of pentacene would contribute to the fabrication of nanostructures and possibly highly oriented pentacene layers by epitaxy for use in electronic devices. To understand the ordering patterns of pentacene ad-layers on metal surfaces, we investigated the energetics between pentacene molecules with and without metal substrates and analyzed its electronic structure. We used a self-consistent first-principles calculation method based on the density functional theory (DFT) within local density approximation (LDA). The localized pseudo-atomic orbitals (PAO) are employed for a real-space numerical basis set, which was suggested by Sankey and Niklewski, and the Troullier-Martins-type pseudo-potential is used. As results, we found that the ordering patterns can be explained by the energetics between pentacene molecules, and the metal substrates appears not to influence too much on the interaction between pentacenes. To investigate the nature of the self-assembled structure, we calculated the total energies of various configurations for the molecule pattern, e.g., side-by-side and head-to-head ordering or on-top stacking. Depending on its direction, extremely different interaction character between two pentacenes is found and explained by its electronic structure analysis.