We fabricate atom-molecule contacts by attaching single Cu atoms to the endgroups of multi-functional molecules on a Cu(111) surface. By means of scanning tunneling microscopy, spectroscopy, and density functional calculations, we find that, due to the localization characteristics of molecular orbitals, the Cu-atom contact modifies the state localized at the endgroup which is in contact with the Cu atom but does not affect the states localized at other parts of the molecule. These results illustrate the contact effects at individual orbitals and offer possibilities to manipulate orbital alignments within single molecules.

**Molecule**: Two terpyridine endgroups linked by a tetraphenyl ethylene bridge - a prototype molecular device

**Technique**: Scanning tunneling microscopy at 5K

**dI/dV** spectra show densities of states. **STS** maps show spatial distribution of molecular orbitals.

**Molecule with Cu Coordinated at its Right End**
- Only the right molecular orbital which is in direct contact with Cu is 0.4 V down-shifted.

**Molecule with Cu Coordinated at its Both Ends**
- The molecular orbitals at both sides are 0.4 V down-shifted.

**Shifting Molecular Orbitals one by one through Single-atom Contacts**