Inorganic Molecular Junctions

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Aviram and Ratner first proposed the idea of molecular electronic devices in 1974.[1] They theorized that a single molecule with a donor-spacer-acceptor (d-s-a) structure would behave as a diode when placed between two electrodes. Thus, a molecular junction is a molecule that bridges two electrodes. Scanning probe microscopy (SPM), developed in 1983[2], allows for the insertion of a molecule into a junction as well as the spectroscopic and topological measurement of the junction formed. Using this and other fabrication techniques, the assembly of molecular-scale junctions is feasible.

One example of an inorganic molecule being chosen to form a molecular junction is that of copper (II) phthalocyanine (CuPc)[3]. Nazin *et al.* employed scanning tunneling microscopy (STM) to form one-dimensional gold chains across a NiAl(100) template by manipulating each gold atom individually into position. The CuPc was then moved into a bridging position across two gold islands and strongly adsorbed by positive interactions between the copper ligands and the gold metal. This nano-structure was confirmed by STM imaging, as shown below in Figure 1.

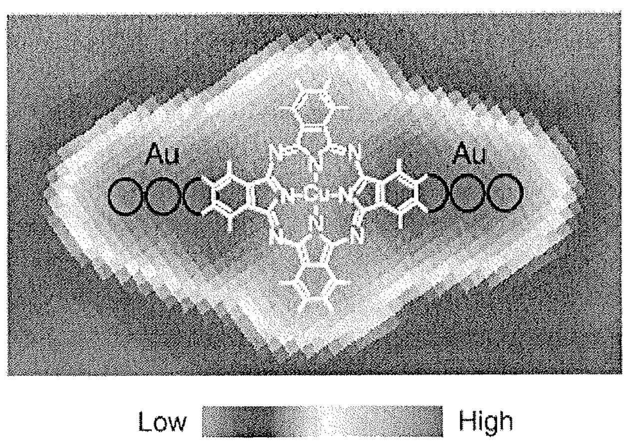

Figure 1

Another method of molecular junction fabrication involves the use of an STM tip as one of the leads. In a representative system, a STM tip was brought into contact with a ferrocene-terminated self-assembled monolayer ($FcC_{11}S$-SAM) (Figure 2).[4] In this experiment, a STM probe both monitored and modulated the current passed through a $FcC_{11}S$-SAM while the potential was varied. Junctions exhibiting NDR (nonlinear differential resistance) were observed. NDR is a common effect and was first exploited in the Esaki diode in 1958.[5] Interpretation of results for molecular devices must be viewed with extreme caution.[6] The current passing through nanosized junctions can experience local temperatures in excess of 1000 K.[7] What's more, it has been known for some time that electric fields can affect the mechanical stability of the STM tip, causing both physical elongations of the tip and surface structure modifications.[8] The observed NDR behavior was most likely caused by other experimental affects.

Transition metal molecules can be selected based upon desired properties. An example is with the use of $[(Me_3tacn)_2V_2(CN)_4(\mu\text{-}C_4N_4)]$ (Me_3tacn= *N,N',N''*-trimethyl-1,4,7-triazacyclononane)[9] (Figure 3) to bridge two gold leads.[10] This molecule was chosen because of it's magnetic properties. The neutral molecule exhibited strong antiferromagnetic behavior between both d^1 vanadium centers and had a net spin (S) of zero.[9] Upon oxidation, the molecule became paramagnetic with a non-zero spin of S=1/2.[10] When the junction was assembled over a gate to form a transistor, the transistor possessed a zero-bias conductance for the oxidized state. This phenomenon, known as the Kondo effect, occurs when the total spin of a molecule is non-zero. The effect arises from the interaction between a magnetic molecule and the two electrodes allowing the electrons to travel across the junction. In contrast, the conductance is blocked when the spin is zero.[11]

In summary, the assembly of individual nanosized junctions has been demonstrated. For practical applications of these devices, a better understanding of the system is still needed; this can be achieved through better characterization of the devices.

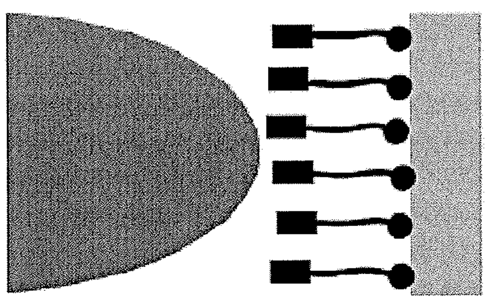

Figure 2

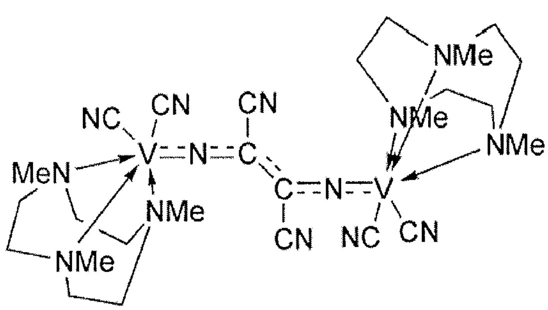

Figure 3

References

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