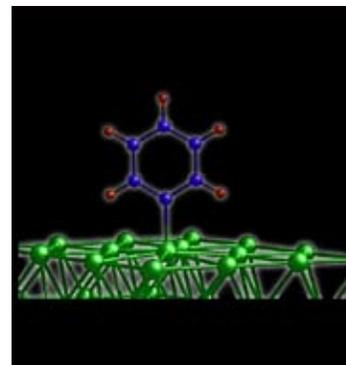
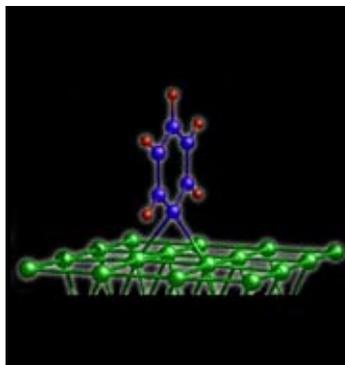
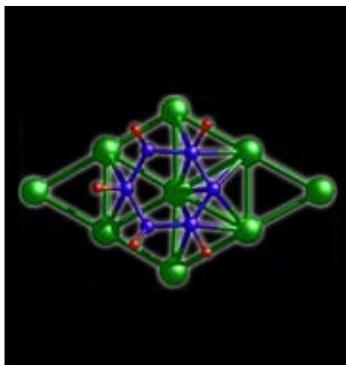




## Aryl Metal Bonding

*Model gives first definitive evidence of chemical bonding between aryl carbon and metal surface.*

If you think that your MP3 player can hold a lot of music now, just wait until molecular electronics becomes the industry standard. Molecular electronics is a burgeoning science that seeks to make electronic devices smaller, faster, and more powerful by replacing the conventional semiconductors used in their circuits with individual molecules. Before that can happen, scientists must determine if reliable electronic connections can be made between the molecules and other circuit elements, such as metallic wires. Oak Ridge National Laboratory researchers De-en Jiang, Bobby Sumpter, and Sheng Dai have used computational simulations to model the bonding between aryl groups—the organic molecules with a flat ring of carbon atoms—and various metal surfaces. Their work yields predictions for the most likely bonding configurations of molecules on various metal surfaces and helps resolve the debate about whether the aryl–metal bond is chemical or physical in nature. This is an important debate for molecular electronics because chemical bonds are ideal electronic connections between molecular circuit elements.



*From left to right, the optimized configurations for chemical bonding between the aryl group and titanium, iron, and gold.*

The research was inspired by the experiments of James Tour, a pioneer in the field of molecular electronics, and his coworkers at Rice University, who recently discovered efficient methods for spontaneously grafting aryl groups to carbon, semiconductor, and metal surfaces. Dai, whose research involves using Tour's grafting methods to functionalize porous carbon materials, proposed the development of the bonding simulations because experiments could not determine if the aryl–metal connection was a chemical covalent bond, in which electrons are shared between the aryl carbon and the metal, or a weaker attraction between oppositely charged parts of the molecule and the metal.

To help resolve the uncertainty, researchers used computational simulations to model the behavior of the electrons responsible for bonding. Their simulations were based on first-principles density-functional theory, which uses quantum physics to determine the interaction properties of the electrons and does not rely on any tunable empirical parameters. The simulations calculated the electron adsorption energies, which are a measure of the bond strength between the aryl carbon atoms and the metal surface. These

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simulations were performed for bonding of C<sub>6</sub>H<sub>5</sub>, the simplest aryl group, on iron, palladium, copper, gold, titanium, and hydrogen-treated silicon.

## Evidence for Chemical Bonding

The calculated adsorption energies strongly indicate chemical bonding between the aryl group and each type of metal. The bond strength decreases from left to right moving across the metals of the periodic table from titanium to copper. The simulations indicate that metals to the left of iron on the periodic table favor bonding with the aryl ring in tilted or flat-lying configurations, while metals to the right of iron favor bonding with the aryl ring oriented upright relative to the metal surface. The calculated tilt angle between the aryl ring and metal surfaces matches reasonably well with the few tilt angles that have been determined by experiment.

The calculations took about 1 month to complete using computers at the National Center for Computational Sciences (NCCS). “This is a very hot topic and we did not want to get scooped. NCCS’s resources enabled us to get this done very quickly,” said researcher Bobby Sumpter.

The results are published in the Journal of the American Chemical Society [128(18), 6030-31 (2006)] as a Communication. These simulations are strong evidence that chemical bonds do indeed form between organic aryl molecules and metal surfaces. Jiang says, “This work is just the beginning. The bonding must be modeled for many other metals, alloys, and oxides.” The researchers hope that this work will catalyze further theoretical and experimental research in the novel science of organic–metal bonding.

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