# CRAFTING MATERIAL SURFACES: ARYL RADICALS IN ACTION

**Avni Berisha**

**Institute, Faculty, Department, University, City, Country**

**Department of Chemistry, Faculty of Natural and Mathematic Science, University of Prishtina “Hasan Prishtina”**

**0000-0002-3876-1345**

|  |
| --- |
| **ABSTRACT**The investigation of molecules in their adsorbed state or when attached to surfaces is a topic of significant interest. Aryl diazonium-derived layers have significant potential in the field of material science, with diverse applications in corrosion protection, sensor fabrication, and photovoltaics. These versatile molecules serves as powerful tools for modifying surfaces and have potential in numerous materials, such as insulators, superconductors, bulk materials, powders, and nanostructured materials [1]. Although extensive experimental studies have explored grafted surfaces, including investigations on stability in challenging conditions, analysis of bonds, evaluation of thermal stability, determination of chemical composition, and measurement of layer thickness, there are still significant gaps in our comprehension. It is important to emphasize that the properties observed in these experiments are collective averages, emphasizing the necessity for additional investigation into intrinsic stability, bond strength, and bond characteristics. In order to tackle these aspects, our approach integrates the capabilities of Density Functional Theory (DFT) calculations [2], Molecular Dynamics (MD) simulations, and empirical data. By utilizing Surface-Enhanced Raman Spectroscopy (SERS), we have detected a specific peak at 387 cm–1, which closely corresponds to the predictions made by theoretical calculations [3]. In addition, through the integration of DFT calculations and selective experiments, we have clarified the fundamental mechanism that governs the spontaneous attachment of diazonium salts onto gold surfaces. Consistent with prior research, aryl radicals display reactivity with the gold surface and the initial grafted layers, resulting in the creation of films that are only a few nanometers thick [4].Carbocations also exhibit interactions with gold, albeit with a slower growth rate and thinner films compared to radicals. The Au-(N=N-Ar) bond formed when diazonium cations directly react with gold is significantly less strong compared to the Au-Ar bond. It is important to highlight that aryl radicals produced from diazonium salts form covalent bonds on different surfaces, such as Graphydine, Borophene [5], and the B12N12 nanocage cluster [6]. The process exhibits inherent spontaneity, which is further supported by transition state calculations conducted to investigate the bonding of the phenyl radical.**References:** [1] Bélanger, D., & Pinson, J. (2011). Electrografting: a powerful method for surface modification. Chemical Society Reviews, 40(7), 3995–4048. doi:10.1039/C0CS00149J[2] Berisha, Avni, & Seydou, M. (2022). Grafting of Aryl Radicals onto Surfaces—A DFT Study - Aryl Diazonium Salts and Related Compounds: Surface Chemistry and Applications. In M. M. Chehimi, J. Pinson, & F. Mousli (Eds.) (pp. 121–135). Cham: Springer International Publishing. doi:10.1007/978-3-031-04398-7\_6[3] Berisha, Avni, Combellas, C., Kanoufi, F., Médard, J., Decorse, P., Mangeney, C., Pinson, J. (2018). Alkyl-Modified Gold Surfaces: Characterization of the Au-C Bond. Langmuir, 34(38), 11264–11271. doi:10.1021/ACS.LANGMUIR.8B01584[4] Berisha, Avni, Combellas, C., Kanoufi, F., Decorse, P., Oturan, N., Médard, J., Pinson, J. (2017). Some Theoretical and Experimental Insights on the Mechanistic Routes Leading to the Spontaneous Grafting of Gold Surfaces by Diazonium Salts. Langmuir, 33(35). doi:10.1021/acs.langmuir.7b01371[5] Berisha, Avni. (2021). First principles details into the grafting of aryl radicals onto the free-standing and borophene/Ag(1 1 1) surfaces.Chemical Physics, 544. doi:10.1016/j.chemphys.2021.111124[6] Berisha, Avni. (2023). Unraveling the electronic influence and nature of covalent bonding of aryl and alkyl radicals on the B12N12 nanocage cluster. Scientific Reports 2023 13:1, 13(1), 1–11. doi:10.1038/s41598-023-28055-8 |
|  |

# Keywords: Aryl radical, Diazonium salt, Surface modification, DFT, Gold surface