

Exploring Aryl Radicals as Multifunctional Agents for (Nano)material Surface Modification: A Comprehensive Review with a Focus on DFT Analysis

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Aryl radicals derived from aryldiazonium cations have emerged as a leading choice for surface modification since their innovative introduction by Professor Pinson in the 1990s [1]. Unlike traditional surface modification agents such as thiols, silanes, and phosphonic acids, aryldiazonium cations offer a more versatile and straightforward method for surface functionalization. This technique proves effective across a broad spectrum of materials [1-4], regardless of their chemical composition or electrical conductivity. In contrast, other agents have limitations: thiols primarily work with noble metals and are ineffective with polymers, while phosphonic acids and silanes are usually limited to surfaces with oxy-hydroxy groups [5].

Herein, we explore the atomistic modelling of diazonium salt grafting mechanisms, energetics, and stability on various substrates, including metals, carbon-based materials, silicones, and phosphorus-based compounds [3]. It examines crucial aspects such as dissociation, the grafting process, and the spectroscopic signatures of diazonium salts. Furthermore, density functional theory (DFT) calculations provide insights into the stability of the formed interfaces, which is challenging to measure directly in experiments that typically capture only the average (collective properties) stability of the layer (e.g., through thermogravimetric analysis). DFT spectroscopic analysis reveals distinctive characteristics of aryl grafting, and when combined with experimental results from vibrational spectroscopies, it allows for the first-time assignment of the Au-C(alkyl) bond [3,6].

References

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