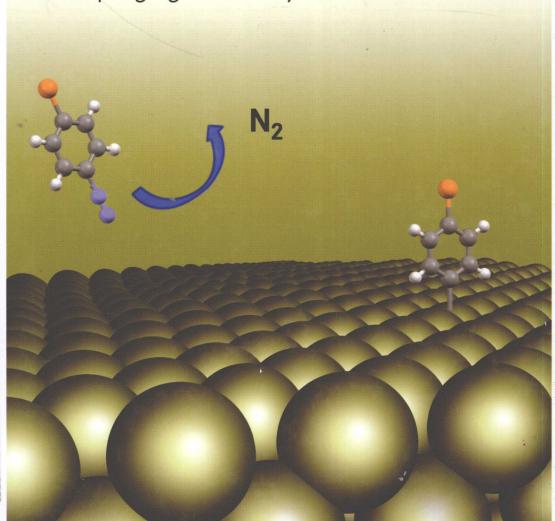
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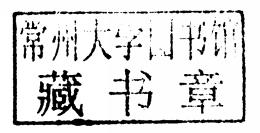
New Coupling Agents in Polymer and Surface Science



Edited by Mohamed Mehdi Chehimi

Aryl Diazonium Salts

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The Editor

Dr. Mohamed Mehdi Chehimi

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To Jean Pinson, with gratitude



Preface

Dear Reader,

The diazotation of compounds has first been described in the mid-19th century by the German chemist Peter Griess. Henceforth, aryl diazonium salts (from the French "diazote", two nitrogen atoms) are commonly used for the synthesis of a large series of organic compounds such as azo dyes, and are thus the object of numerous articles and book chapters or sections. However, the study of the surface and interface chemistry of these salts remained sparse despite its interest in modifying materials surfaces. For example, it was shown in 1958 that the reaction of aryl diazonium salts with mercury electrodes results in electrografting of aryl groups on this liquid metal with formation of phenylmercuric chloride and diphenylmercury (Elofson, R.M., *Can. J. Chem.*, 1958, **36**, 1207–1210, doi: 10.1139/v58-174; see also Chapter 1). Later in 1961, aryl diazonium salts were proposed as coupling agents in histochemistry for the labeling of enzymes (Burstone, M.S., Weisburger, E.K., *J. Histochem. Cytochem.*, 1961, **9**, 301–303, doi: 10.1177/9.3.301).

In modern surface science, Jean Pinson and co-workers described, in 1992, the mechanisms of the reaction between aryl diazonium salts and glassy carbon electrodes resulting in surface-tethered aryl groups. Provided that the functional group, in para position of the diazonium, is reactive, it becomes possible to graft polymers, enzymes, catalysts, etc. Since then, the two last decades (1992-2012) witnessed a quantum jump in the number of publications pertaining to surface chemistry and applications of aryl diazonium salts. The interest in using these compounds obviously lies in their ease of preparation, rapid reduction by a large range of methods and strong aryl-surface covalent bonding. Grafted aryl groups can be used as such in order to impart new physicochemical properties, or can serve as coupling agents for additional species. The applications concern electronics, electrocatalysis, sensors, nanocomposites, drug delivery, to name but a few, as testified by over 3000 articles and reviews, book chapters, and chapter sections. Several processes involving aryl diazonium salts were also patented and industrial products, though not too many, are on the market (see Chapter 14). Despite these extraordinary academic and industrial achievements, there is no comprehensive book dealing with the fundamental aspects of surface and interface chemistry of the diazonium salts and their use as surface modifiers and coupling agents. The

book that you are holding in your hands fills this gap in 14 self-contained chapters written by acknowledged experts in their respective fields.

One can distinguish three main parts: fundamental and analytical aspects of diazonium-modified surfaces (Chapters 1–4); applications of diazonium salts in electrocatalysis, polymer science, sensors and biosensors, and electronics (Chapters 5–11). The third part concerns related or alternative organic molecules (e.g. amines, triazenes, vinyl, ethynyl, Grignard reagents) for surface treatment in general (Chapter 12) and for the more applied molecule-silicon electronics, in particular (Chapter 13). The book finishes by a contribution summarizing patents and industrial applications of the surface chemistry of aryl diazonium salts and related compounds (Chapter 14).

Dear Reader, we would like to thank you for choosing our book. As you will appreciate, the surface chemistry of diazonium salts and related compounds has progressed at a remarkable pace. The gap between the academic research on diazonium salt surface chemistry and its industrial applications has already been filled although this topic of surface science and technology is still in its infancy. Whether you are a student, technician, engineer, teacher or researcher; expert or newcomer, it is hoped that the information provided by all contributors will open new horizons.

As an editor, it has been a very exciting experience to collaborate with acknowledged experts from the five continents. I should like to thank them all for kindly accepting my invitations to contribute to this adventure. I am also very much indebted to all reviewers for their guidance. I am grateful to my colleague, Dr. Abderrahim Boudenne (Université Paris Est Créteil, France), for his remarkable help when I started the book project. I must also add here that I, personally, as well as my students, have learned a lot from Professor Jean Pinson. I have enjoyed his teaching of chemical kinetics and magneto-chemistry when I was one of his third year students in 1981 at University Paris 7; it is both and an honor and a privilege to have him as a colleague 30 years later. It therefore gives me great pleasure to dedicate this book to my former professor of chemistry and actual colleague and friend Jean Pinson.

This experience has been intense and exciting over almost 2 years. It would not have been possible to put the book in its final form, in such a short period of time, without the continuous support, encouragement, love, and patience of my daughter Inès, my son Selim, and my wife Heger.

March 2012

Mohamed Mehdi Chehimi

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