Preface

Prebiotic Photochemistry: From Urey–Miller-like Experiments to Recent Findings

Mankind has always been fascinated by the mystery of the origins of life. We could almost imagine that the human being and questions like "where do we come from?" were born together. Also, because of such an inextricable *liaison*, the complexity of this topic is certainly one of the highest ever touched by our minds. It is not surprising, hence, that chemical evolution on primordial Earth, Earth-like planets and in the whole Universe, with the subsequent origin of the first living structures, represent one of the most intriguing and controversial enigmas faced by contemporary science.

Within the huge framework composing the research on the life's origins, prebiotic chemistry plays a crucial role in the understanding of the very first steps of the whole story. Prebiotic chemistry is a branch of chemistry which investigates the affordable reaction networks connecting the available and most plausible chemical precursors into pre-biologically and biologically relevant compounds which are present in actual organisms, such as, *e.g.*, amino acids, sugars, nucleobases and amphiphilic molecules.

A fundamental question that arises from prebiotic chemistry is intrinsically connected to the identification of the chemical environment where the original prebiotic syntheses took place. Nowadays, there exist many proposals on the abiogenesis of the fundamental molecules of life, which are supported by a plethora of empirical data both for the exogenous delivery (space dust, meteorites and comets) and for the endogenous synthesis (hydrothermal vents, atmospheric lightning, warm ponds, and so on and so forth).

The milestone experiment of the whole realm of prebiotic chemistry is the so-called "Miller–Urey experiment", dating back to the 1950s and which described the formation of one of life's building blocks (amino acids) when

Comprehensive Series in Photochemical and Photobiological Science No. 20
Prebiotic Photochemistry: From Urey–Miller-like Experiments to Recent Findings
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Published by the Royal Society of Chemistry, www.rsc.org

electric discharges were passed through inorganic mixtures of simple molecules such as methane, ammonia, water and hydrogen. Of course, electric discharges do not represent the unique source of energy capable of triggering prebiotically relevant chemical reactions which shape the routes connecting the inorganic and the organic worlds.

Another extremely powerful and widespread source of energy which could have played a key role in driving chemical reactions towards the emergence of life on Earth and Earth-like planets is light. After all, it is very hard to think of the idea of life without evoking the concept of light. In fact, electromagnetic radiation not only carries the daily-proven ability of sustaining life as we know it but also holds many peculiarities which render it an extremely efficient – and sometimes selective – means for the promotion of prebiotic reactions in earthly environments and at extreme conditions such as those experienced in comets and other interstellar bodies in outer space.

In a nutshell, these are the reasons behind the onset of an entire research branch known as *prebiotic photochemistry*, this being the main subject of the present book. As mentioned, being the possible energy sources to life and scenarios highly multifaceted and almost never inextricable from each other, the topics faced in this volume inevitably touch also investigations where light plays a co-role in assisting prebiotically relevant chemical transformations. As a consequence, in this book, the reader will find not only a conspicuous number of contributions describing the state-of-the-art developments tightly bound to the field of prebiotic photochemistry, but also a series of advanced studies where light, playing only a side role, is assisted by other energy sources and selective conditions/media. On the other hand, in addition to this very general subdivision, this volume can also be divided into a number of ways that could be useful and instructive to experts in related fields as well as to beginners. Being an exponentially growing research branch, indeed, we do hope that the present book will serve as a beacon for future generations approaching this fascinating – and full of novelties – line of research.

In Chapter 1, (Giannetto), the role of light underlying the onset of living systems is examined from the point of view of physics (quantum electrodynamics) and photochemistry, with a strong holistic and philosophical accent.

In Chapter 2, (Arumainayagam *et al.*), the authors critically analyse the energetic processes triggered by light in cosmic ices. In particular, some of the dominant mechanisms for the extraterrestrial synthesis of prebiotic molecules are carefully investigated.

The comprehension of the chemistry leading to the synthesis of N-bearing organic molecules and macromolecules in the upper atmosphere of Titan is addressed in Chapter 3, (Balucani and Skouteris).

Chapter 4, (Carrasco and Gautier) summarizes the contributions of early Earth atmospheres to sustain the emergence of life influencing both the climate and prebiotic chemical synthesis through photochemistry.

In Chapter 5, (Szabla), the photostability of primary components of biomolecules and selective UV-assisted chemical routes to these compounds is treated from the standpoint of theoretical chemistry, time-resolved spectroscopy and organic synthesis.

The key role played by formamide as chemical precursor of potentially biogenic molecules is addressed in Chapter 6, (Saladino *et al.*) under a photochemical scenario.

In Chapter 7, (De Vries *et al.*), the response to UV radiation of excited state dynamics of alternative combinations of the canonical nucleobases is carefully explored.

The roles of comets in prebiotic photochemistry along with that of cometary dust in the interaction between electromagnetic radiation and the reactivity of solid-state molecules is delineated in Chapter 8, (Rotundi *et al.*).

In Chapter 9, (Iatì *et al.*), the hypothesis of an extraterrestrial origin of biomolecular chiral homogeneity, through a mechanism of asymmetric photolysis in space is examined.

The potentialities of accurate quantum-chemical computations to interpret the gas-phase reactivity at work in the interstellar medium is discussed in Chapter 10, (Puzzarini and Barone).

The unexpected absence of complex organic species in the cold gas in protoplanetary discs is discussed in Chapter 11, (Cecchi-Pestellini *et al.*).

In Chapter 12, (Ferus *et al.*), the authors summarize the current state-of-the-art research results concerning the impact-induced reprocessing of atmospheres, planetary surfaces and the synthesis of molecules relevant to prebiotic chemistry.

The plausible journey of the life of glycine, from its likely formation in the interstellar medium (ISM), passing through its transportation and release on a primitive Earth by bombardment of micro-asteroidal grains, up to its final evolution in the form of polypeptide, as described by quantum chemical simulations is presented in Chapter 13, (Ugliengo *et al.*).

A new energetic concept for the origin of life is formulated in Chapter 14, (Sponer *et al.*) by comparing the energetics of a wide scale of synthetic reactions that could have led to nucleobases, nucleotides and oligonucleotides in primordial environments.

Ultimately, we wish for this volume to be a useful pedagogical tool for a broad variety of researchers working in all those intriguing fields embracing the origins of life. The aim of our book is indeed that of being impactful for any research area that relies on prebiotic photochemistry and, more in general, on prebiotic chemistry to guide – by setting the current state-of-the-art – experimental, theoretical and computational studies of the near future.

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