ACCOUNTS
of chemical research

GUEST EDITORIAL

Origins of Chemical Evolution

Chemical evolution includes the capture, mutation, and propagation of molecular information and can be manifested as coordinated chemical networks that adapt to environmental change. The robustness of a chemical network depends on the diversity of its membership, which establishes the probability for the successful selection of superior chemical species and populations. A dynamic exchange of network component structures and assemblies, via both covalent and noncovalent associations, is fundamental for the network's ability to learn, to capture and integrate information about an environment that ensures the network's future response to similar conditions, as an inherent part of chemical evolution. In considering the origins of chemical evolution or discovering the simplest molecular systems capable of promulgating intelligent behavior, we acknowledge that merely defining the terms learning, intelligence, and evolution at a molecular level remains a significant part of our challenge in this *Accounts of Chemical Research* issue.

The origins of life on Earth, the remarkable result of chemical evolution through emerging self-assembly into ever-increasing hierarchical complexity in structure and function, remains one of the greatest research challenges of our time. Our understanding of reaction dynamics and energetics, growing insight in dynamic combinatorial systems, increasing refinement of models for the structures of supramolecular assemblies, and expanding knowledge of the cooperative interactions of biopolymers in present-day cells suggest that the timing of this special issue could not be more appropriate. We therefore begin our discussion with the small molecules, including sugars, nucleosides, lipids, and amino acids, that were likely members of a diverse and rich prebiotic inventory and the clear role the emergence of chirality of these building blocks plays in the selection and amplification processes from which modern biochemistry appeared. The discussion extends to the general concept of molecular complementarity, which underpins the development of all supramolecular assemblies, and certainly those containing hydrogen-bonded or metal-coordinated complexes capable of self-replication through dynamic response to fluctuating environmental stimuli.

The Darwinian threshold required for appearance of the biological cell underscores the development of "self" versus "non-self" in these chemical networks. The barriers that define dynamic chemical systems as uniquely self must be physically and kinetically selective to permeability, primarily of nutrient molecules that maintain network viability. The approaches presented in this issue evaluate roles of atmospheric flux, lipid-like compartmentalization, and self-replicating protocells in creating nanoscale assemblies that could provide the necessary features of a cellular system. As the components of cellular structure accrete, the ability to transduce energy from the environment in order to maintain dynamic functions removed from thermodynamic equilibrium is a critical step along the path to complex cellular life. Experimental systems that execute photochemically driven redox cycling and that generate chemical gradients to impel systems toward synthetic complexity and ordered structure are also described. The role of noncovalent interactions and new approaches to creating dynamic covalent assemblies is further explored in the emergence of both digital and analog information arising from molecular assemblies.

These diverse approaches to deconvolution and reintegration of the origins of the cell, projected in collaboration through the lens of chemical evolution, suggest a remarkable degree of intrinsic molecular intelligence that guide the bottom-up emergence of living matter. However, this idea of molecular intelligence is certainly not new. Charles Darwin imagined a chemically rich "warm pond" from which evolution originated, and his idea was published almost 100 years before the duplex structure of DNA was proposed. A population of simple molecules, storing and copying information to ensure their own survival prebiotically, argues that intelligent behavior is not restricted to complex genomes but is an inherent property of matter. Darwin's hypothesis further predicts the emergence of new intelligent materials, ones not limited to what can be

Published on the Web 12/18/2012 www.pubs.acs.org/accounts
10.1021/ar300266q

deduced from biology's "archeological" remnants but even more diverse and exotic realms of dynamic chemical systems that might never have been explored by extant biochemistry.

While our objective is to decipher the evolutionary rules that directed the transition from inanimate matter to life, we recognize that the march of molecular history likely had many pathways. Accordingly, this issue circumscribes the functional concepts, leveraging Nature's platforms for molecular information, using its existing chemical inventory or libraries, and, with selective and judicious tinkering along the way, elaborates the basic rules of bottom-up self-assembly guided by both digital and analog molecular recognition systems. In addition, the diversity in approaches to understanding and employing chemical evolution is as important as the diversity in chemical composition required to promulgate evolution itself and suggests that collaboration among these diverse approaches to gaining insights into chemical evolution and working toward the interfaces among them will be extraordinarily rich with opportunities. Although not an exhaustive survey, we hope that this special issue will inspire the broader scientific community to elaborate and expand efforts in this research realm and to seek synchronicity with systems biology as the top-down complementary approach to deciphering the origins and function of living matter, to look forward to how we can design and construct new intelligent materials that address the grand challenges we face as a society, and to look outward, to other worlds that may harbor life in ways that such insights into chemical evolution may help us better understand, anticipate, and recognize.

David Lynn
Emory University
Guest Editor

Cynthia Burrows
University of Utah
Guest Editor

Jay Goodwin
Emory University

Anil Mehta
Emory University