J. Yamada
T. Sugimoto (Eds.)

TTF Chemistry

Fundamentals and Applications of Tetrathiafulvalene

Kodansha Springer

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Fundamentals and Applications of Tetrathiafulvalene

With 262 Figures, 196 Schemes, 75 Charts and 47 Tables

Kodansha Springer

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Foreword

Large streams from little fountains flow
Tall oaks from little acorns grow—David Everett

In this volume, the very patient and gifted editors, Jun-ichi Yamada and Toyonari Sugimoto, have achieved a remarkable collection of fundamental aspects of "TTF Science". This book is also a testament to the enormous growth of TTF chemistry alone from 1973 until 2002. There are 17 chapters dedicated, *inter alia*, to the synthesis of symmetric, unsymmetric, heteroatom-substituted, halogenated, stable radical-substituted, dimeric (simple, fused or cyclophane-type), oligomeric (linear, macrocyclic and dendritic) and TTF-acceptor linked molecules for special applications. With the exception of Chapter 16 (rectifiers, photovoltaics, nonlinear optics), the emphasis of the book is strictly on chemistry in general and synthesis in particular. To badly quote the David Rueben book (and Woody Allen's movie), this remarkable TTF Chemistry book you are holding in your hands contains "everything you always wanted to know about TTF chemistry but [were] afraid to ask". This makes this monograph unique in the field because in the past, compendia dedicated to TTF science have always had a large physics component.

An organic metal? An organic superconductor? An organic solar cell? Any scientist or engineer living in the early part of the 20^{th} century, up to the 1960's would have scoffed at the idea. But, starting in the 1970's, a special, small sulfur heterocycle was the gateway to organic metals, superconductors and semiconductors and will very likely have a role to play in organic ferromagnets (see Chapter 6 by J. Nakazaki and A. Izuoka) and organic solar cells (see Chapter 16 by N. Martín and J. Garín).

The radical cation $TTF^{(+\bullet)}$ was first published under its official IUPAC name, bis-1,3-dithiolium "$BDT^{(+\bullet)}$" in 1970 but derivatives of its neutral form had already been prepared by Prinzbach, Takamizawa and Hünig. In the meantime, Cowan had been exploring the properties of fulvalene-iron complexes and their mixed valence properties so that when the Johns Hopkins group published their first paper on the temperature dependence of the conductivity of the TCNQ salt of bis-1,3-dithiolium radical ion, they labeled it (TTF)(TCNQ) [rather than (BDT)(TCNQ)] and, except for Chapter 13 by K. Takahashi, where the old name needed to be resurrected, the less "legal" name TTF stuck for perpetuity. Hünig and Coffen had also made the heterocycle but did not give it an unusual name. The fact that $TTFCl_n$ was discovered to be a highly conducting solid led to the formation of the first organic metal in 1973 as well as a, never substantiated, claim for superconducting fluctuations above 57 K in this solid in the same year. The last two publications were the catalyst which initiated the growth of interest in TTF in the chemistry and physics communities.

One could trace the study of all modern organic conductors, including conducting polymers, back to the principles learnt from TTF and its salts. Many of today's "players" in conducting polymers were either trained with TTF-based systems or developed TTF-based semiconductors, metals and superconductors before extending their work to conducting polymers.

It is clear that the chemistry of TTF is a vibrant and active part of the organic chemistry scene. It has sparked the imagination of that rare breed of organic chemists, heterocyclic chemists and sulfur chemists who are interested not only in the synthesis of a molecule but also in its applications. In practically every issue of the most important chemistry journals today one can find a paper containing some aspect of TTF-based science. One of the most recently fashionable trends in organic materials science research is that of "molecular machines" and molecular-based computers. Here TTF is also playing an important role [see C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath and J. F. Stoddart, *J. Am. Chem. Soc.*, **123**, 12632 (2001)].

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Preface

The synthesis of tetrathiafulvalene (TTF) independently reported by the three research groups of Wudl, Coffen and Hünig during the period 1970–1971 inaugurated the TTF era, and TTF chemistry has been undergoing remarkable development. The first great milestone was marked in 1973 by the discovery of metallic behavior in the charge-transfer (CT) complex composed of TTF and tetracyanoquinodimetane (TCNQ). This discovery stimulated work on new donor compounds related to TTF, and, simultaneously, considerable attention was focused on the field of organic conductors, which has its origin in the discovery of the conducting perylene-bromine complex by Akamatsu, Inokuchi and Matsunaga in 1954. The next two striking milestones occurred with the discovery of superconductivity in the CT salt of tetramethyltetraselenafulvalene (TMTSF) in 1980, followed by that in the CT salt of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) in 1983. Needless to say, the TMTSF and BEDT-TTF donors belong to the TTF family. Since then, great momentum has been sustained by organic chemists, inorganic chemists, physical chemists, solid-state physicists, theoretical physicists and materials scientists. A large number of metallic and superconducting organic materials are now known, and new TTFs, TTF-type compounds and their CT materials continue to be reported week by week. Recently, attention has also been directed to the novel magnetic and optical properties that CT materials based on TTFs and related compounds can display.

The study of design and synthesis of new TTF-based systems to provide organic materials with more interesting and exciting solid-state properties is an obvious first step. However, no single volume has so far compiled review articles pertaining to various aspects of TTF chemistry authored by prominent organic chemists, although some collections of data and a number of individual review articles have been published. The aim of this volume is to highlight the chemistry of functionalized TTFs (Part I), dimeric TTFs (Part II) and 1,3-dithiol-2-ylidene donors (Part III) and the applications of TTFs from the molecular level to the supra- and macromolecular levels (Part IV), which will be very useful to specialists and nonspecialists, with the aim of interpreting current advances in TTF chemistry. We hope that this volume will serve not only as a reference work for a broad audience, but also as a review citing much of the extensive literature related to this field.

We are grateful to all the invited contributors who readily consented to write chapters of this book, and are convinced that every chapter will make a contribution as a guideline to further progress in this interdisciplinary and important field of modern materials chemistry. We sincerely thank Professor Fred Wudl who, as a pioneer of TTF chemistry, kindly contributed the foreword to this book. Thanks are due to Mr. Ippei Ohta of Kodansha Scientific Ltd. for very good cooperation in the editing this book.

We are most thankful to all those who have contributed their time and effort to the work cited in this book. Finally, generous financial support by Grant-in-Aid for Publication of Scientific Research Results from Japan Society for the Promotion of Science is gratefully acknowledged.

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Jun-ichi Yamada
Toyonari Sugimoto

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