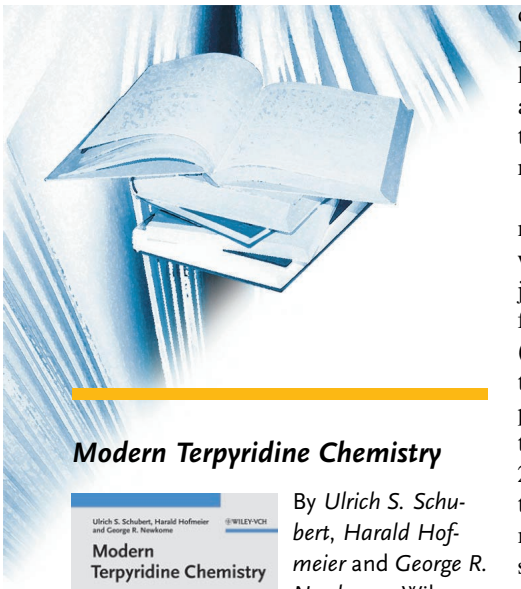
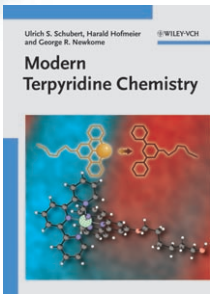


Modern Terpyridine Chemistry



By *Ulrich S. Schubert*, *Harald Hofmeier* and *George R. Newkome*. Wiley-VCH, Weinheim 2006. 229 pp., softcover € 85.00.—ISBN 978-3-527-41475-1

This book aims to give an overview (but not a comprehensive treatment) of the chemistry of the ligand 2,2′:6′,2″-terpyridine and its derivatives, and to introduce the reader to the plethora of applications that these compounds find in supramolecular and nanoscale chemistry. To preface the remainder of this review, I can state at the outset that the authors succeed in these aims, and the result is a scientifically rigorous text that is at the same time readable and readily approachable by a good Masters student or a beginning doctoral student. The authors are leading scientists who are actively involved in this area, and they write with expertise and knowledge.

To complete the raw statistics, the book comprises seven chapters in 230 pages, covering topics that include the synthesis and coordination chemistry of 2,2′:6′,2″-terpyridine derivatives, and applications in supramolecular and polymer chemistry. It finishes with brief surveys of the use of these ligands in more complex three-dimensional architectures, and in the modification of surfaces. One can always complain that one's pet topic is omitted from a short monograph of this type, but in general all important areas of 2,2′:6′,2″-terpyridine chemistry are covered, and the reader is given the key entries to the literature to allow deeper study. The text and graphics are cleanly presented, and the authors make sensible use of a minimal amount of color artwork.

Why should anyone wish to read a monograph on this class of compounds, which for many years were thought to be just the exotic "big brother" of more familiar ligands such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline? In part, the answer to this question is given on page 3 of the text, where a histogram of the numbers of publications on 2,2′:6′,2″-terpyridine (tpy) from 1990 to the present time reveals a near-exponential increase, to the current level of something over 300 per year. Another answer comes from the fact that a wide variety of substituted 2,2′:6′,2″-terpyridine derivatives can be synthesized easily in good yields and in laboratory-scale quantities. The final answer comes from the unique properties of metal complexes of these ligands: topologically linear connectivity across a metal center, useful redox and photophysical properties that complement but differ from those of $\{M(bpy)_3\}$ species, high thermodynamic stability, widely varying kinetic properties ranging from "granite-inert" to "ephemerally labile", and $\{M(tpy)_2\}$ motifs that are usually achiral. Indeed, it was this latter feature that was responsible for $\{M(tpy)_2\}$ becoming the motif of choice for the assembly of diads and triads, metallopolymers, metallostars, and metallodendrimers. The $\{M(bpy)_3\}$ motif is chiral, existing in Δ and Λ enantiomeric forms, and compounds containing multiple $\{M(bpy)_3\}$ centers will be mixtures of diastereoisomers unless stereospecific syntheses are utilized—in contrast, species containing multiple achiral $\{M(tpy)_2\}$ motifs occur as single isomers.

Today, much of the emphasis in 2,2′:6′,2″-terpyridine chemistry lies in the preparation of (highly) functionalized derivatives, and the first chapter provides a timely and broad survey of synthetic methods, with a good listing of available substituents and substitution patterns. The newcomer to heterocyclic chemistry might sometimes be in for a little head-scratching in elucidating mechanisms, and the authors have made an understandable decision not to get side-tracked into these issues. Little, if anything, is said about the vast amount of solid-state structural information that is available for the free ligands. This would perhaps have helped with the varying depictions of 4′-hydroxy-2,2′:6′,2″-terpyridines and their 2,2′:6′,2″-terpyridin-4′(1′*H*)-one tautomers—the solid-state X-ray crystallographic analysis shows that both species are present in the crystal.

The discussion of the metallo-supramolecular chemistry of 2,2′:6′,2″-terpyridines is, perforce, somewhat selective, but I cannot personally fault any of the examples that have been included. The division of material between the chapters dealing with polymers, supramolecular chemistry, and three-dimensional functional structures is necessarily somewhat arbitrary. As a result of this organization, the casual reader might not immediately appreciate the relationship between cyclic and polymeric complexes, although this is explicit within the text. This is, however, something of a carping criticism, as I cannot think of a better way to divide the material, especially considering that one of the authors is a leading expert in metallopolymer chemistry.

For me, the most interesting chapter is the final one, which deals with surface modification by 2,2′:6′,2″-terpyridines and their complexes. It is here that the reader who is not an expert in 2,2′:6′,2″-terpyridine chemistry can see both the potential of the system and some applications. This chapter moves beyond the "laboratory world" of supramolecular chemistry to the "real world" of interfacial chemistry and functional systems that are subjected to the challenges of aggressive chemical environments and a need for long-term performance. I think it is a tribute to 2,2′:6′,2″-terpyridine chemists that one of the two ruthenium complexes of choice for Grätzel-type dye-sensitized solar cells incorporates 2,2′:6′,2″-terpyridine-4,4′,4″-tricarboxylic acid. It is also a challenge for the future, as the large-scale preparation of this ligand is still a frustrating, and usually low-yielding, process.

The authors of the book are "organic" chemists by training, and this shows in the chapter dealing with the coordination chemistry of 2,2′:6′,2″-terpyridine, which I, as an inorganic chem-

ist, found to be the least satisfactory. In particular, there is no real discussion of the kinetic properties of the metal complexes. This is critical to the supramolecular chemistry—in essence, labile metal ions allow rapid self-assembly in reversible reactions, leading to thermodynamic products, whereas inert metal centers lead to kinetic products in which the ligands "stay where you put them".

Naturally, no book is perfect, and this is no exception, but it would be disingenuous to detract from this positive review with a list of trivial errors and omissions. However, if a second edition is planned, it would be worthwhile to check the references, both for accuracy in the authors' names and for the matching of citations to the text.

This book should be on every supramolecular chemist's shelf and on the reading list for every modern course in heterocyclic chemistry.

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