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Book Review

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Carbon-rich compounds: from molecules to materials

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663 pp; price £115.00/EURO 172.50
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Despite the ever-increasing interest in new carbon-rich materials and carbon allotropes, no doubt inspired by the discovery of the fullerenes and carbon nanotubes, there is a paucity of monographs summarizing current developments in the chemistry of these fascinating compounds. Volumes 196 and 201 of the Topics in Current Chemistry series (Springer), subtitled *Carbon Rich Compounds I* and *II*, respectively, contain focussed state of the art reviews from the late 1990s. This new book, written by experts in their respective research fields, aims to update the reader on recent developments in carbon-rich chemistry, with a view toward material applications. The reviews are founded on synthesis; most chapters offer a selection of representative experimental procedures should the inspired reader wish to get some first-hand experience of the preceding chemistry.

The chapters appear to be in no particular order, although Johnson and Haley's useful historical perspective on the discovery and classical syntheses of carbon-rich compounds up to 1970 is logically placed as Chapter 1. The remaining 12 chapters cover a broad range of topics including monodisperse and polymeric organic and metal–organic wires, macrocycles and polycyclic aromatic hydrocarbons, through to fullerenes and their redox chemistry.

Chapters 2 and 10 both deal with metal–organic assemblies where the metal centres are linked through (primarily conjugated) organic linkers. Electronic conduction in photoactive metallowires and the structural factors that influence energy and charge transfer are discussed in detail by Harriman and Ziessel (Chapter 2). Yam and Tao (Chapter 10) choose to focus on organometallic alkynyl and polyynyl complexes of Re(I), Pt(II), Cu(I), Ag(I) and Au(I) with an emphasis on photophysical properties. Complexes prepared in Yam's laboratory predominate, thus resulting in a review that is short of comprehensive but nevertheless instructive of the versatility of metal-containing carbon-rich chromophores.

Meier (Chapter 11) reviews synthetic approaches toward oligophenylenevinylene and oligophenyleneethynylene chromophores with well-defined lengths. The relationships between structure (conjugation length, *cis–trans* isomerism, donor–acceptor type) and photophysical behaviour (linear/nonlinear absorption, emission) are clearly presented.

Strategies for the solid-state topochemical polymerization of diacetylenes, triacetylenes, dienes and trienes are described by Fowler and Lauher in Chapter 5. The crystal packing alignment of the unsaturated monomers is shown to be a critical factor in successful polymer synthesis. Host–guest approaches to controlling crystal packing are helping to understand what is still largely a serendipitous process. The synthesis, structure and reactivity of 1,3-butadiyne units are further discussed in Chapter 7. Inspired by the earlier topochemical polymerization of diacetylenes, Gleiter and Werz develop the chemistry of cycles containing these rigid linear four carbon units. The cavities formed in the crystals of some of the cycles have been shown to host small aromatic guest molecules.

The lengthy Chapter 6 by Campbell and Tykwinski provides a thorough introduction to the latest innovations in the design and synthesis of chiral carbon-rich macrocycles. Synthetic schemes rely heavily on acetylenic coupling reactions with achiral and chiral building blocks. When geometrical constraints and/or steric interactions between achiral units provide a conformational twist, helical chirality can be afforded. Chirality is induced in metal-containing macrocycles with chelating or bridging binaphthyl-based ligands.

Miljanić and Vollhardt (Chapter 4) use aromaticity arguments to explain the chemistry of [*N*]phenylenes, the parent congener being biphenylene ($C_{12}H_8$) comprising two 'aromatic' benzene rings annelated though an 'antiaromatic' cyclobutadiene ring. Metal-catalysed synthetic strategies for the preparation of [*N*]phenylenes with a wide range of geometries and sizes are described in detail. Structural, magnetic and energetic properties are presented and compared with computational studies.

The synthesis, electronic properties, self-assembly and device applications of all-benzenoid polycyclic aromatic hydrocarbons (PAHs) are presented in an excellent overview by Wu and Müllen (Chapter 3). Since the authors' development of high-yielding routes to soluble large all-benzenoid PAHs, efforts to control molecular ordering on surfaces and in the bulk have resulted in significant progress toward the goal of incorporation into organic electronic devices. In contrast to the mostly planar all-benzenoid PAHs, Sygula and Rabideau describe the synthesis and chemistry of curved PAHs (Chapter 12). An historical perspective on the synthesis of these so-called buckybowls is presented, beginning with early low-yielding routes, often employing harsh reaction conditions, through to impressive non-pyrolytic syntheses of corannulenes. Larger curved PAHs derived from or containing corannulene fragments have now been prepared, along with a $C_{60}H_{27}Cl_3$ PAH that serves as a pyrolysis precursor to C_{60}, albeit in poor yield. Transition metal complexation and alkali metal reduction of buckybowls conclude the discussion.

The following chapter continues more generally on the theme of alkali metal reduction of carbon-rich compounds. Sternfeld and Rabinovitz describe in detail the formation of anions and radical anions of buckybowls, π-conjugated monocyclic systems, cyclophanes and fullerenes. The importance of NMR and EPR spectroscopies for the characterization of reduced species is stressed. Special attention is given to the reduction of fullerenes due to their unique ability to reversibly accept up to six elections.

At the other end of the spectrum, Chapter 9 by Kitagawa, Murata and Komatsu looks at functionalized fullerene cations, an aspect of fullerene chemistry that is much less well explored when compared with neutral addition products and the above-mentioned anions. The second part of the chapter outlines synthetic approaches to open-cage fullerenes as host molecules for small guests and as precursors to endohedral fullerenes.

Finally, Schreiner provides a nice overview of computational chemistry as applied to carbon-rich structures (Chapter 8). He outlines the advantages, disadvantages and limits of the various theoretical methods at the disposal of chemists, supported by examples to illustrate application to carbon-rich compounds. Following proper validation of a method, the

ability to reliably predict the properties of yet to be synthesized compounds holds great benefits for materials scientists.

The book has been carefully edited with very few typographical errors detected and a reasonably consistent style used throughout (Chapter 11 most notably deviates from the standard). The numerous figures and schemes are clearly presented. While the book is a collection of quite focussed, molecular structure-based topics under the banner of carbon-rich chemistry, the writing is at a level that is accessible to those chemists new to the field. The breadth and detail of most chapters places the book somewhere between an advanced textbook in organic materials chemistry and a reference guide with ample citation of the primary literature.

Carbon-rich Chemistry: From Molecules to Materials is a welcome new title, filling a significant hole in the literature. It is heartily recommended to those with an interest in the synthesis and characterization of carbon-rich compounds as new materials.

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