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Review

Boron clusters-based metallodendrimers

Clara Viñas, Francesc Teixidor, Rosario Núñez *

Institut de Ciència de Materials de Barcelona (CSIC), Campus U.A.B., E-08193 Bellaterra, Spain

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ABSTRACT

This review includes a compilation of different types of star-shaped molecules and dendrimers decorated with boron clusters, carboranes or metallacarboranes, at their periphery. Dendrimeric platforms, such as PAMAM, carbosilane, poly(aryl-ether), among others, have been functionalized with a different number of small metallacarboranes, *nido*-carboranes or cobaltabisdicarbollide clusters following diverse methodologies. In general, all these structures are high-boron content molecules, and for those that carry *nido*-carboranes and alkaline metals, are also soluble in water. Most of these compounds have been proposed as highly promising boron delivery agents for the BNCT of tumors, particularly for malignant brain tumors. Nevertheless, other applications such as catalysts, optoelectronic devices, drug delivery systems, and others can be envisaged.

Prof. Clara Viñas *graduated in Chemistry at the Universitat Autònoma de Barcelona in 1975 and in Pharmacy at the Universitat de Barcelona in 1980. She worked as a pre-doctoral student at the Prof. Rudolph's laboratory at The University of Michigan for a year. Back to Barcelona, she worked for industry and later moved to Laboratori Municipal de Sabadell where she became the director to work on food and environmental control. She got her PhD in Pharmacy under the supervision of Prof. F. Teixidor at the Universitat de Barcelona in 1990. She joined the staff of the C.S.I.C. as Tenured Scientist in 1991. She promoted to research scientist in 2002 and to research professor in 2006. Her research interests are in the synthesis of novel boron compounds, carboranes and metallacarboranes, to be used for future medicinal applications.*

Prof. Francesc Teixidor *obtained his PhD in Chemistry in 1979 from Universitat Autònoma de Barcelona under the supervision of Prof. Heribert Barrera and pursued postdoctoral research with Prof. Ralph Rudoph at University of Michigan. He was appointed Assistant Professor at Universitat Autònoma de Barcelona in 1982. In 1987 he got an Associate Professor position at the Spanish Council for Scientific Research (CSIC) at the Materials Science Institute (ICMAB). Since 1999 he holds a Full Professor position at the same Institute. His research interests are in the chemistry, particularly in the formation of B–C and B–P bonds, and application of boron cluster compounds in molecular materials with particular emphasis in energy.*

* Corresponding author. Tel.: +34 93 5801853; fax: +34 93 5805729.
E-mail address: rosario@icmab.es (R. Núñez).

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Dr. Rosario Núñez *was graduated in Chemistry from Universidad de Granada. She carried out her thesis at the ICMAB (CSIC) under the supervision of Prof. Clara Viñas and received her PhD from Universitat Autònoma de Barcelona in 1996. After that, she worked as a postdoctoral fellow with Profs. Bruno Boury and Robert Corriu at the Université de Montpellier II. In 1999, she joined the ICMAB as a fellow staff doctor to work in the LMI managed by Prof. Francesc Teixidor. From 2001 she has a permanent position as a tenured scientist. Her research interests are the synthesis and study of properties of carborane derivatives, as well as the preparation of carboranyl-containing molecular and hybrid materials.*

Contents

1. Introduction

Dendrimers are hyperbranched and mono-dispersed macromolecules [1], with well-defined size, molecular weight, internal connectivity and specific number of end groups which provide special properties and a great variety of different applications [2,3]. The incorporation of metals in dendritic structures generates metallodendrimers [4], which show substantial structural diversity and properties, to be used in a wide range of applications, such as catalytic, redox, magnetic, molecular electronics, energy conversion, sensing, medical and photo-optical materials [5,6].

The *closo*-1,2-$C_2B_{10}H_{12}$ carborane cluster, known as *o*-carborane, o-$C_2B_{10}H_{12}$ (Chart 1), is chemical and thermally stable with a rigid three-dimensional structure [7]. The $C_{cluster}$–H protons in carboranes can be easily removed by strong bases generating nucleophile anions that have the ability to react with a wide range of electrophilic reagents [8]. The removal of a B^+ vertex leads to the formation of anionic *nido*-species with different electronic properties to their *closo*-precursors. The unique stability and geometrical properties of the *o*-$C_2B_{10}H_{12}$ have suggested these compounds and their derivatives to be used as building blocks for novel molecular materials with properties that cannot be achieved with organic hydrocarbon compounds.

The cobaltabisdicarbollide, $[(3,3'\text{-Co-}(1,2\text{-}C_2B_9H_{11})_2]^-$ (Chart 1) [9], is a boron-rich monoanionic cluster, that has extraordinary chemical and thermal stability, lipophilicity [10], weakly coordinating character [11] and low nucleophilicity. To functionalize this metallacarborane, two main ways can be used, by linking functional groups on the cluster carbon atoms [12] or on the cluster boron atoms [13]. Few examples of direct substitution on the carbon atoms are known. One of the most recent report has been the synthesis of the synthon C_c-silyl-substituted cobaltabisdicarbollide, Cs [1,1′-μ-SiMeH-3,3′-Co(1,2-C2B9H10)2] [12c], which allows the preparation of boron-rich polyanionic macromolecules *via* hydrosilylation reactions [14] of vinyl and allyl terminated dendrimers. Substitution at boron is mainly performed by the synthesis of the zwitterionic compound [3,3′-Co(8-$(C_2H_4O)_2$-1,2-$C_2B_9H_{10}$)(1-

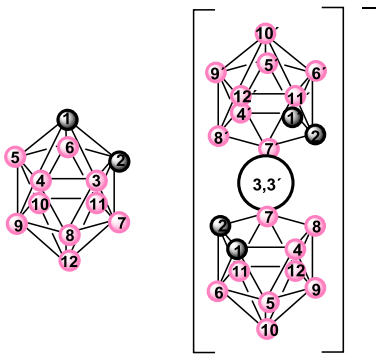

Chart 1. Icosahedral heteroboranes with their vertex numbering: neutral *closo*-carborane *o*-$C_2B_{10}H_{12}$, and cobaltabisdicarbollide $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$.