

# Chemistry of Organic-Hybrids

Synthesis and Characterization  
of Functional Nano-Objects



Edited by **Bernadette Charleux, Christophe Copéret & Emmanuel Lacôte**

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# CHEMISTRY OF ORGANO-HYBRIDS

## Synthesis and Characterization of Functional Nano-Objects

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*Edited by*

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# CHEMISTRY OF ORGANO-HYBRIDS





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# PREFACE

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Science has moved and will increasingly move toward the molecular echelon. From biology and medicine to materials—and even the very French specialty, gastronomy!—many disciplines are claiming the “molecular” label. It features an understanding of events on a molecular level and the ability to control them through design and synthesis. The latter are thus keys to the future of many fields.

As practitioners of the field, we believe that tremendous opportunities are being created through the ability to design and synthesize novel functional tools—catalysts, devices from probes to batteries, photovoltaics, diagnostic and therapeutic agents, etc.—involving hybrid materials, made of ever more complex organic, organometallic and inorganic molecules linked to active nano-scaled supports (nanoparticles, clusters, polymers and biopolymers, etc.). In other words, molecular architectures certainly stand at the crossroad of most of the major present fields of research, provided their synthetic requirements are adapted to those of objects outside their traditional boundaries.

We define an organic hybrid as a material made by linking polymeric, carbon-rich or inorganic material to organics (small molecules or macromolecules). Our aim is to provide readers—organic synthetic chemists interested in applying their skills to function-oriented synthesis, non-organic chemists wishing to introduce molecular complexity to their field, students trying to make sense of objects that span over several fields of the curriculum—with a general overview of the diversity of solutions that organic, inorganic, and polymer synthetic chemists, chemical biologists, and materials scientists have come up with to control functions through the covalent attachment of specific supports to endlessly variable molecular architectures.

Each new material has specific requirements (availability, stability, surface functionality, etc.) that limit the options available for chemists to graft the desired function-laden molecules. It is also a challenge to determine whether a determined bonding between the entities has been achieved. This in turns generates new questions and opportunities for research and applications. Thus, this book emphasizes two main topics: synthesis and characterization.

The science of hybrids is growing at a galloping speed, so it is impossible, frustrating and in the end futile to pretend to be exhaustive. Rather, we have selected a few key items across the hybrids’ family to illustrate the concept and approaches that can be replicated for other classes of supports. This is also why we have minimized the illustration of the properties of the materials as this is depicted in scores of reviews, generally at the expense of the presentation of the nuts and bolts of the synthesis, which the present book seeks to redress. We however explain what property(ies) the molecular template introduces or modifies as this drives the design of the functionalization itself and the methods used to achieve the goal.

In a nutshell, the authors have answered in the most concise way possible the following questions: *Why and how to do it? And how to prove that you did it?* That is, after a brief introduction on why go for a strategy involving hybrids—how this affects properties, or generates new ones—two issues are addressed, namely (i) what are the synthetic strategies and reactions required and (ii) how can one tell the reactions worked? Are there specific analytical techniques to support the claims? It is very interesting and enriching to see how each of them has interpreted these very simple constraints!

We have subdivided the book into 13 chapters, by classes of supports grouped in small clusters. The first cluster of chapters focuses on carbon-based materials, illustrating three different and complementary angles. Cécilia Ménard-Moyon has illustrated the functionalization of carbon nanotubes; Iban Azcarate, David Lachkar, Emmanuel Lacôte, Jennifer Lesage de la Haye, and Anne-Laure Vallet focused on the chemistry of graphenes; Maria Gunawan, Didier Poinot, Bruno Domenichini, Peter Schreiner, Andrey Fokin, and Jean-Cyrille Hierso on the contrary focused on the chemistry of the very compact nanodiamonds.

After this carbon-rich foray, the second cluster deals with inorganic materials. In the first two chapters of this part, the functionalizations of titania (Laurence Rozes, Loïc D'Arras, Chloé Hoffman, François Potier, Niki Halttunen, and Lionel Nicole) and zirconia (Marc Petit and Julien Monot) are a perfect illustration of the different options a single change in chemical composition of the support can bring. The two other chapters are devoted to large surface area materials with two different perspectives: Flavien Morel, Xiaoying Xu, Marco Ranocchiari, and Jeroen van Bokhoven examine the highly porous MOFs, while Richard Brutchey, Zeger Hens, and Maksym Kovalenko discuss semiconducting nanoparticles.

The third cluster is devoted to three classes of biopolymers, with a representative example of each main natural building block. Michel Arthur and Mélanie Etheve-Quelquejeu show the challenges of nucleic acids modification; Divya Agrawal and Christian Hackenberger those of modified protein synthesis; and Maxime Guitet, Mickaël Ménand, and Matthieu Sollogoub those of the selective transformation of cyclodextrins.

The final cluster examines polymers: how one can selectively functionalize artificial polymers (Anja Goldmann, Mathias Glassner, Andrew Inglis, and Christopher Barner-Kowollik), as well as how one can couple artificial polymers with biopolymers (Paul Wilson, Julien Nicolas, and David Haddleton). Finally, Anne-Marie Caminade, Béatrice Delavaux-Nicot, and Jean-Pierre Majoral present the specific reactivity challenges of dendrimers, which are from two worlds, macromolecules and molecules... hybrids within hybrids.

We thank all the authors for their contribution and we hope the reader will enjoy the various and varied contributions as much as we did.

Bernadette Charleux  
Christophe Copéret  
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# CONTENTS

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<b>Preface</b>	<b>vii</b>
<b>Contributors</b>	<b>ix</b>
<b>1 COVALENT ORGANIC FUNCTIONALIZATION AND CHARACTERIZATION OF CARBON NANOTUBES</b> <i>Cécilia Ménard-Moyon</i>	<b>1</b>
<b>2 FUNCTIONALIZED GRAPHENES</b> <i>Iban Azcarate, David Lachkar, Emmanuel Lacôte, Jennifer Lesage de la Haye, and Anne-Laure Vallet</i>	<b>36</b>
<b>3 NANODIAMONDS: EMERGENCE OF FUNCTIONALIZED DIAMONDoids AND THEIR UNIQUE APPLICATIONS</b> <i>Maria A. Gunawan, Didier Poinot, Bruno Domenichini, Peter R. Schreiner, Andrey A. Fokin, and Jean-Cyrille Hierso</i>	<b>69</b>
<b>4 TITANIA-BASED HYBRID MATERIALS: FROM MOLECULAR PRECURSORS TO THE CONTROLLED DESIGN OF HIERARCHICAL HYBRID MATERIALS</b> <i>Laurence Rozes, Loïc D'Arras, Chloé Hoffman, François Potier, Niki Halttunen, and Lionel Nicole</i>	<b>114</b>
<b>5 FUNCTIONALIZATION OF ZIRCONIUM OXIDE SURFACES</b> <i>Marc Petit and Julien Monot</i>	<b>168</b>
<b>6 FUNCTIONAL METAL-ORGANIC FRAMEWORKS: SYNTHESIS AND REACTIVITY</b> <i>Flavien L. Morel, Xiaoying Xu, Marco Ranocchiari, and Jeroen A. van Bokhoven</i>	<b>200</b>
<b>7 SURFACE CHEMISTRY OF COLLOIDAL SEMICONDUCTOR NANOCRYSTALS: ORGANIC, INORGANIC, AND HYBRID</b> <i>Richard Brutchey, Zeger Hens, and Maksym V. Kovalenko</i>	<b>233</b>
<b>8 COVALENT ORGANIC FUNCTIONALIZATION OF NUCLEIC ACIDS</b> <i>Michel Arthur and Mélanie Etheve-Quelquejeu</i>	<b>272</b>

<b>9</b>	<b>CHEMOSELECTIVE PROTEIN MODIFICATIONS: METHODS AND APPLICATIONS FOR THE FUNCTIONALIZATION OF VIRAL CAPSIDS</b>	<b>299</b>
	<i>Divya Agrawal and Christian P. R. Hackenberger</i>	
<b>10</b>	<b>CYCLODEXTRINS–METAL HYBRIDS</b>	<b>349</b>
	<i>Maxime Guitet, Mickaël Ménand, and Matthieu Sollogoub</i>	
<b>11</b>	<b>POST-FUNCTIONALIZATION OF POLYMERS VIA ORTHOGONAL LIGATION CHEMISTRY</b>	<b>395</b>
	<i>Anja S. Goldmann, Mathias Glassner, Andrew J. Inglis, and Christopher Barner-Kowollik</i>	
<b>12</b>	<b>POLYMER–PROTEIN/PEPTIDE BIOCONJUGATES</b>	<b>466</b>
	<i>Paul Wilson, Julien Nicolas, and David M. Haddleton</i>	
<b>13</b>	<b>HYBRID MATERIALS BUILT FROM (PHOSPHORUS) DENDRIMERS</b>	<b>503</b>
	<i>Anne-Marie Caminade, Béatrice Delavaux-Nicot, and Jean-Pierre Majoral</i>	
	<b>Index</b>	<b>527</b>

# COVALENT ORGANIC FUNCTIONALIZATION AND CHARACTERIZATION OF CARBON NANOTUBES

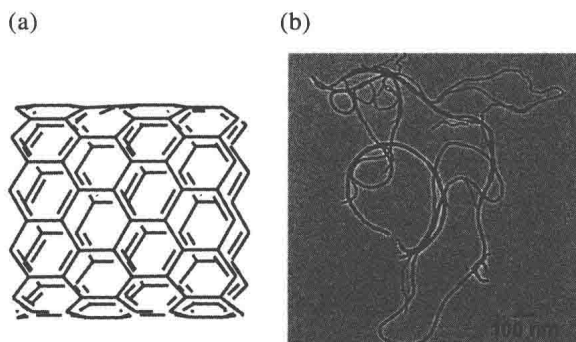
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## 1.1 INTRODUCTION

More than 20 years ago, Iijima reported the structural morphology of carbon nanotubes (CNTs) by use of high-resolution transmission electron microscopy (HRTEM) and electron diffraction [1]. A CNT can be defined as a graphene sheet rolled up to form a cylinder (Fig. 1.1a). CNTs can be classified into different types: single-wall CNTs (SWCNTs), double-wall CNTs (DWCNTs), and multi-wall CNTs (MWCNTs) depending on the number of layers. SWCNTs have diameters ranging from 0.7 to 2 nm and lengths up to several micrometers, while MWCNTs have diameters from a few to tens of nanometers and lengths up to a few micrometers. Hence, the structure of CNTs is characterized by a high aspect ratio (i.e., ratio between length and diameter). Approximately two-thirds of as-produced SWCNTs are semiconducting, whereas one-third is metallic. CNTs contain defects in their structure, such as vacancies, and five- or seven-membered rings that induce curvature, as illustrated in the transmission electron microscopy (TEM) image in Figure 1.1b.

The breadth and range of research involving CNTs has expanded greatly over the past years. Indeed, CNTs possess unique electronic, mechanical, and thermal properties



**Figure 1.1.** Schematic representation of a SWCNT (a) and TEM image of MWCNTs (b).

that can be exploited for potential applications in a variety of fields from materials science [2], molecular electronics [3], photovoltaic devices [4] to nanomedicine [5]. However, CNTs have poor solubility in all solvents due to strong intermolecular cohesive forces among the nanotubes that form bundles, thus hampering full exploitation of their properties and presenting obstacles to their practical applications. Therefore, functionalization is required for manipulating and processing CNTs by inducing exfoliation, increasing dispersibility, and giving the possibility to associate molecules with specific properties to nanotubes.

Functionalization can be classified into two categories: covalent and noncovalent derivatization, the latter relying on hydrophobic,  $\pi$ - $\pi$ , and/or electrostatic interactions [6–8]. Covalent functionalization can be achieved by oxidation of defect sites of CNTs and subsequent derivatization of the generated carboxylic acid groups. Other methods are based on halogenation, cycloaddition reactions, or direct additions of highly reactive species on the nanotube sidewall. Grafting functional groups on the nanotube surface in a covalent manner allows to obtain stable conjugates with desired properties by tailoring the physicochemical properties of the CNTs. Depending on the level of functionalization, the electrical conductivity of the CNTs can be significantly altered. It is of high importance to rigorously characterize functionalized CNTs. For this purpose, different spectroscopic, microscopic, and thermal techniques can be used for morphological, structural, and elemental analysis of functionalized CNTs.

This chapter is focused on covalent methodologies for nanotube functionalization. Section 1.2 is dedicated to the different chemical strategies used for covalent functionalization of CNTs, while Section 1.3 describes the analytical techniques for characterization of functionalized CNTs. Finally, Section 1.4 contains some concluding remarks.

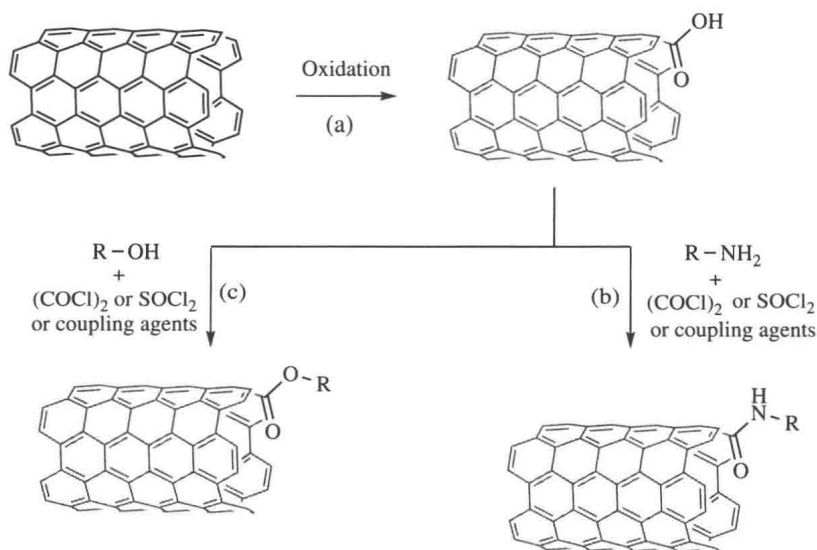
## 1.2 COVALENT FUNCTIONALIZATION OF CARBON NANOTUBES WITH ORGANIC MOLECULES

### 1.2.1 Defect-Site Chemistry

Among various surface functionalization techniques, amidation or esterification of oxidized CNTs is probably the most extensively used to prepare soluble materials either in

organic solvents or in water and for linking a wide range of molecules [9]. Generally, oxidation of CNTs is performed by treatment with strong acids such as nitric acid [10, 11], sulfuric/nitric acid mixture [10], or with other strong oxidizing agents ( $\text{H}_2\text{SO}_4/\text{KMnO}_4$  [12] or  $\text{OsO}_4$  [13]). The oxidative treatment, in particular when assisted by sonication, usually induces shortening of the CNTs [10], but also frequently causes nanotube damage, limiting their use as mechanical and electrical reinforcements. Among treatments using strong acids, low-power sonication of MWCNTs in nitric acid followed by treatment with hydrogen peroxide was found to minimize nanotube damage [14]. Many research groups have studied the chemical nature of the oxygenated moieties (e.g., carboxylic acids, carbonyls, hydroxyls) [15] introduced on the nanotube surface by different techniques such as infrared (IR) spectroscopy [16] and thermogravimetry [15]. Oxidized CNTs are mainly decorated with carboxylic groups, as suggested by the pioneering work of the group of Smalley who derivatized the carboxyl functions with thiolalkylamines by amidation [10]. The CNTs bearing thiol moieties were labeled with gold nanoparticles and visualized by atomic force microscopy (AFM). Gold nanoparticles were found mainly at the nanotube ends. By using scanning tunneling microscopy (STM), Prato and coworkers visualized alkyl chains introduced by amidation of carboxylic acid functions, confirming that oxidation of CNTs occurs mainly at the nanotube tips [17].

Oxidized CNTs have been widely used as precursors for further covalent derivatization via amidation or esterification reactions, with amine or alcohol derivatives, respectively (Fig. 1.2). The carboxylic acid functions have to be pre-activated via the formation of acyl chlorides using oxalyl or thionyl chloride, followed by the addition of the appropriate amine or alcohol. Alternatively, the amidation can be performed by using the carbodiimide coupling chemistry. In this case, the carboxyl groups are



**Figure 1.2.** Oxidation of CNTs (a) and, amidation (b) and esterification of oxidized CNTs (c). For clarity, a SWCNT segment is shown with only a single added functional group.



treated with *N*-hydroxy succinimide (NHS) or 1-hydroxybenzotriazole (HOBt) in the presence of a carbodiimide, usually *N,N*-dicyclohexylcarbodiimide (DCC) or 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC). The corresponding esters are then displaced by amine or hydroxyl functions to form the amide or ester bonds, respectively.

A range of molecules with various properties have been linked on the CNTs by this method, including several organic molecules [18, 19], chromophores with optoelectronic properties [20], bioactive molecules [21–23], or polymers [24, 25]. To provide evidence of the ester bond formation in soluble CNTs functionalized with lipophilic or hydrophilic chains, defunctionalization was performed by acid- or base-catalyzed hydrolysis, leading to recovery of the starting insoluble CNTs [26]. In another study, esterification between oxygenated functions at the tips of single oxidized SWCNTs has been exploited to form rings of nanotubes with a narrow size distribution according to AFM [27].

## 1.2.2 Halogenation

**1.2.2.1 Fluorination.** Fluorination has been one of the first chemical methods developed to functionalize CNTs [28]. Most strategies involve elemental fluorine at high temperatures (up to 600°C) (Fig. 1.3a) [29–33]. The best temperature conditions are between 150°C and 400°C. The highest degree of functionalization was found to be one fluorine atom for every two carbon atoms according to elemental analysis [34].

Alternative conditions implying  $\text{CF}_4$  plasma treatment have also been developed [35, 36]. Due to rehybridization of a high number of  $\text{sp}^2$  carbon atoms to  $\text{sp}^3$ , the resulting fluoronanotubes are insulating.

Fluorination drastically enhances the reactivity of the nanotube sidewalls. Therefore, derivatization of fluoronanotubes by nucleophilic substitution reactions is possible (Figs. 1.3b–1.3d) [37]. Indeed, a variety of nucleophilic reagents has been used such as alkyl magnesium bromides (Grignard reagents) [38] and alkyllithium derivatives [39]. Fluoronanotubes have also been reacted with several amines [40], diamines [41], diols [42], or amino alcohols [42].

**1.2.2.2 Bromination.** A few methods for bromination of CNTs have been recently reported using various conditions. DWCNTs have been brominated by elemental bromine using microwaves, leading to a mild alteration of the  $\pi$ -conjugated sidewall of the nanotubes according to Raman spectroscopy (5–8 wt% of Br) (Fig. 1.4a) [43]. Alternatively, bromination of DWCNTs using  $\text{Br}_2$  vapor at room temperature results in 5–6 at% bromine concentration [44]. Plasma using gaseous bromine has been applied for the functionalization of SWCNTs. The treatment is very efficient as one bromine atom per two carbon atoms is introduced on the nanotube surface in these conditions [45]. The bromo-functionalized nanotubes have been further derivatized by nucleophilic substitution with amine derivatives. Elemental bromine in the presence of a Lewis acid or dibenzoylperoxide as radical initiator allows to functionalize MWCNTs with 10–22 at% Br [46]. As alternative, SWCNTs have been brominated via a mild reaction using *N*-bromosuccinimide (NBS) (Fig. 1.4b) [47]. NBS readily decomposes into bromine and succinimide radicals with the help of light, heat, and ultrasound. The