Tetrahedron Letters 57 (2016) 4651–4663

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Digest paper

Metal–organic hybrid architectures built from functionalized fullerenes and metal ions or clusters

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ARTICLE INFO

Article history:
Received 23 June 2016
Revised 26 August 2016
Accepted 28 August 2016
Available online 30 August 2016

Keywords:
Fullerenes
Hexakisadducts
Metal complexation
Metal–organic frameworks
Structure elucidation

ABSTRACT

The well-established exohedral functionalization chemistry of fullerenes, with C_{60} as the most prevalent example, provides easy access to a variety of functionalized carbon nanostructures with great structural diversity and unusual spatial orientation of the attached moieties. Therefore, such molecular nanostructures can be identified as promising building blocks for the design and synthesis of three-dimensionally cross-linked molecular architectures giving rise to novel topologies which would not be accessible from other organic building blocks. Within this perspective, we would like to give an overview on recent progress in the design and synthesis of metal–organic hybrid architectures composed of highly functionalized fullerene derivatives as organic connectivity centers and metal ions or clusters as cross-linking nodes. The ultimate goal of these investigations is the precise control of three-dimensional arrangements of fullerene units in the solid state and the implementation of such carbon derivatives as organic connectivity centers into porous functional materials such as metal–organic frameworks (MOFs).

Contents

Introduction

Fullerenes as spherical carbon clusters are an intriguing class of materials due to their unprecedented electronic and chemical properties.[1] Furthermore, their well-established exohedral functionalization chemistry[2] gives easy access to a great variety of derivatives possessing molecular geometries which are generally not accessible for small organic building blocks. In particular, octahedral hexakisaddition[3–5] of malonate addends to [60]fullerene constructs a unique platform featuring the precise spatial arrangement of up to twelve functional groups with icosahedral symmetry. Based on this approach, C_{60} has been widely utilized as a molecular branching point[6] in the design and synthesis of numerous dendritic nanostructures in recent years. Post-synthetic modifications of privileged intermediates by click chemistry,[7–10] Mitsunobu[11] or cross-coupling[9] reactions further showcase the modularity of this approach. Selected examples include the formation of mixed [3:3][12] or [5:1][8,13,14] hexakisadducts, fullerene sugar balls as potent virus inhibitors,[15–18] polyelectrolytic fullerene dendrimers,[19,20] supramolecular systems,[21,22] a dendritic photosynthetic model compound,[23] and fullerene-containing liquid crystals.[24] Despite the fact that the majority of systems reported so far have been predominantly studied in solution, the implementation of such highly functionalized organic building blocks as organic linkers into extended solid-state frameworks is also highly tempting. Over the last two decades, metal–organic frameworks (MOFs)[25,26] have emerged as a fast growing area of materials

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http://dx.doi.org/10.1016/j.tetlet.2016.08.082
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science with potential applications ranging from gas sorption[27] to sensing[28] to heterogeneous catalysis.[29] However, the vast majority of organic linkers being integrated into these hybrid materials are based on di- and tritopic rigid molecules. In contrast, the implementation of building blocks possessing higher degrees of functionality and/or unusual geometries might enhance both the scope and diversity of such framework materials. However, such concepts have been explored to a much lesser extent so far.[30] In this perspective, we aim to give an overview over recent progress regarding the implementation of highly functionalized fullerene moieties as organic connectivity centers in crystalline hybrid complexes and polymers by cross-linking appropriately functionalized derivatives with metal ions or clusters.

Direct metal–fullerene interactions

The most straightforward approach to synthesize metal–fullerene hybrid materials is to utilize the tendency of pristine fullerenes to readily react with elementary metals. Shortly after the discovery of the first fullerene-metal complexes such as $(\eta^2\text{-C}_{60})\text{Pt(PPh}_3)_2$,[31] various metal–organic polymers have been synthesized by reactions of C_{60} with different metal precursors. Prominent examples include composite materials containing transition metals such as Pd_nC_{60},[32] Ru_3C_{60},[33] and Pt_nC_{60}[34] from the groups of Itoh, Schlögl, and Vugman, respectively. However, such polymers usually lack crystallinity and in many cases, only their stoichiometric compositions are known. Despite considerable covalent interactions in these structures compared to fulleride salts[35] which are readily formed with more electropositive metals, such compounds will not be further discussed in this overview. Instead, we would like to refer the interested reader to recently published excellent reviews on these topics.[35–37] More sophisticated binding motifs are realized in fullerene-containing sandwich complexes in which two fullerene molecules are directly connected through the metal cluster. The first example in this regard was realized by the group of Choi with the dimeric complex $\{\text{Rh}_6(\text{CO})_5(\text{dppm})_2(\text{CNR})\}\{\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}[(\text{C}_{60})_2]\}$[38] ($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$, dppm = bis(diphenylphosphino) methane, see Fig. 1a for X-ray structure). The two fullerene moieties are bridged by an octahedral Rh_6-cluster, with one $\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60}$ being coordinated to the Rh(1, 2, 3) triangle together with one additional isocyanide and one dppm ligand. The second $\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60}$ molecule is coordinated to the Rh(1, 4, 5) triangle accompanied by two additional dppm ligands. Hence, the Rh1-atom is coordinated to both of the face-capping C_{60} ligands in a η^2-mode, which is the first example of two fullerenes complexed by a single metal center. Cyclovoltammetric measurements revealed strong electronic communication between the two C_{60} molecules. Subsequently, various metal–fullerene sandwich complexes have been reported containing W and Mo,[39] Ir,[40] Co[41,42] and Ni[43] among other metal centers. Whereas

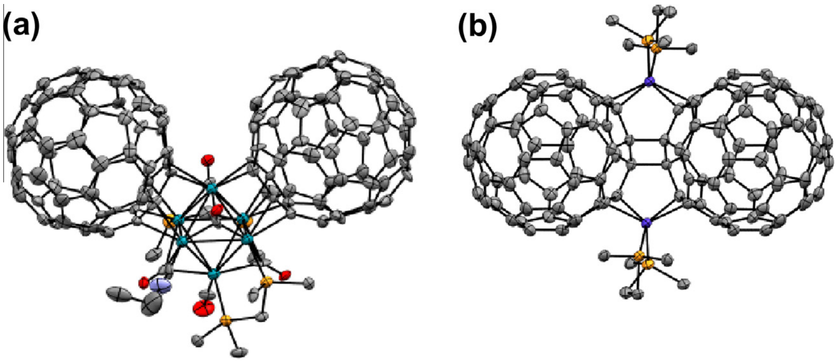

Figure 1. (a) Crystal structure of the first fullerene-metal sandwich complex $\{\text{Rh}_6(\text{CO})_5(\text{dppm})_2(\text{CNR})\}\{\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}[(\text{C}_{60})_2]\}$;[38] (b) crystal structure of dimer $\{\text{Co(dppe)}\}_2\{\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}\eta^2\text{:}\eta^2\text{-}[(\text{C}_{60})_2]\}$.[42] Thermal ellipsoids set to 50% probability, phenyl groups except *ipso*-carbon atom of dppm, dppe, and CNR are omitted for clarity; color code: C, gray; O, red; P, orange; N, orchid; Rh, teal; Co, blue.

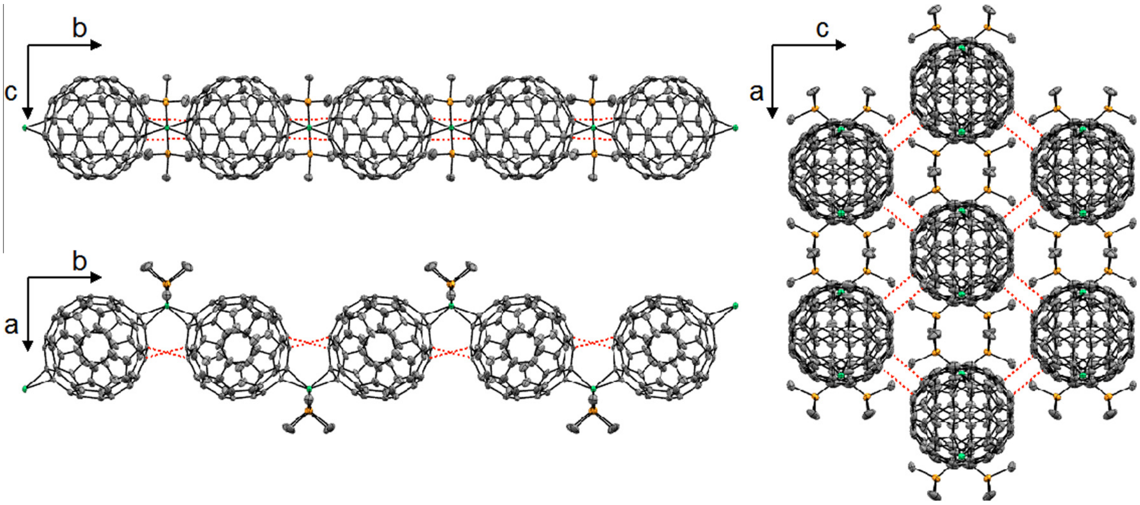

Figure 2. Three different views of metal–organic polymer $\{[\text{Ni(Me}_3\text{P})_2](\mu\text{-}\eta^2,\eta^2\text{-C}_{60})\}_\infty$. Color code: C, gray; P, orange; Ni, green; short interfullerene C–C-distances are marked in red.[44]