JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

Nanorods versus Nanovesicles from Amphiphilic Dendrofullerenes

Antonio Muñoz,[†] Beatriz M. Illescas,[†] Macarena Sánchez-Navarro,[†,‡] Javier Rojo,[*,‡] and Nazario Martín[*,†,§]

[†]Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain
[‡]Glycosystems Laboratory, Instituto de Investigaciones Químicas, CSIC - Universidad de Sevilla, Américo Vespucio, 49. Isla de la Cartuja 41092 Sevilla, Spain
[§]Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Campus UAM, Cantoblanco, E-28049, Madrid, Spain

S Supporting Information

ABSTRACT: Three new amphiphilic dendrofullerenes endowed with 4, 8, and 16 carboxylic groups have been efficiently prepared by using a click chemistry methodology. These amphiphilic fullerene derivatives aggregate forming micelles, nanorods, or hollow vesicles depending on the concentration and on the solid substrate.

The unique physical and chemical properties of fullerenes have been successfully used in the development of two main scientific areas, biological applications[1] and functional materials.[2] The first research topic requires working with water-soluble biocompatible materials, which has generated the evolution of strategies to overcome the natural hydrophobic character of fullerenes.[3] One of these strategies implies the use of dendritic fullerene derivatives.[4] On the other hand, the most promising applications of fullerene-based materials are related to the development of organic electronic devices, such as field effect transistors (OFETs) or solar cells (SCs).[5] In both fields, the study of self-organization of fullerene derivatives to obtain functional supramolecular architectures is nowadays an important scientific challenge.[6] Thus, for instance, the investigation of the aggregation of fullerene containing amphiphiles has led to the formation of micelles, vesicles, and other structures.[7] In some cases, this aggregation can be controlled by an external stimulus, such as pH, which could be useful for the design of targeted drug delivery systems.[8] Nakamura and co-workers have reported the formation of bilayer vesicles with small water permeability coefficient from nonpolar/polar/nonpolar amphiphiles constituted by the potassium complexes of penta-substituted fullerene anions.[9]

From the point of view of the construction of functional materials, it has been proved that a change in the morphology of the material can give rise to the modification of its physicochemical properties. Thus, the chiroselective assembly of a chiral porphyrin−fullerene dyad has demonstrated a better ambipolar charge-carrier mobility for nanofibers obtained from the enantiopure compound than for the spherical aggregates resulting from the racemic dyad.[10] Guldi, Torres, Prato, and co-workers have reported the increased lifetime of the photogenerated charge-separated (CS) state resulting when a phthalocyanine−C_{60} amphiphilic derivative (ZnPc−C_{60}) is ordered into one-dimensional nanotubes. The ordered nanotubular structure showed a lifetime of the CS state ($\tau \sim 1.4$ ms) 6 orders of magnitude longer than that obtained for the monomeric ZnPc−C_{60} dyad ($\tau \sim 3.0$ ns).[11]

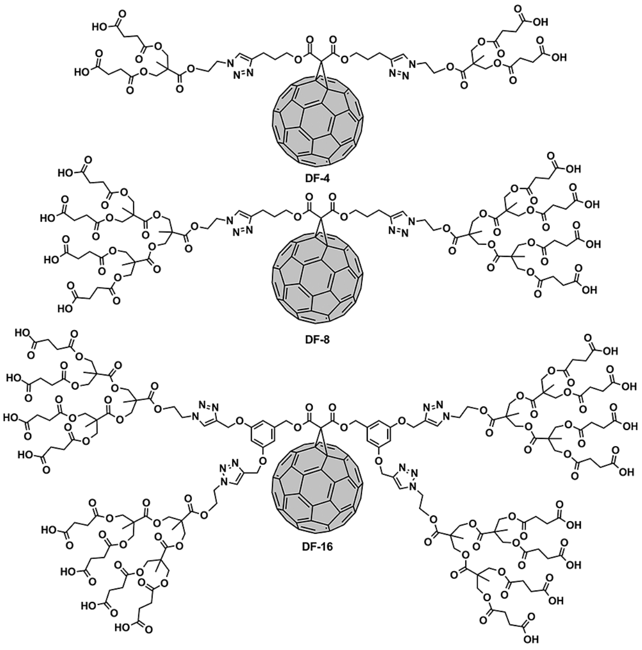

Figure 1. Structure of new amphiphilic dendrofullerenes (DF) (number refers to the content of carboxylic groups).

Recently, the utility of copper-catalized azide−alkyne cycloaddition (CuAAC) reaction to obtain highly functionalized fullerene derivatives has been demonstrated.[12] In this paper, we report on the synthesis of new amphiphilic dendrofullerenes (Figure 1) by using the above-mentioned click-chemistry methodology. The study of the aggregation behavior of such fullerene-based amphiphiles has shown the formation of nanorods, micelles, or vesicles depending on the nature of the solid substrate employed for the deposition of the dendrimeric fullerene solutions or on the concentration of this solution.

The synthesis of fullerene dendrimers was carried out by Huisgen Cu-catalyzed coupling reaction of alkyne functionalized fullerene derivatives (**1** and **2**, see Supporting Information (SI)) with azide substituted dendrons endowed with a variable number

Received: July 20, 2011
Published: September 14, 2011

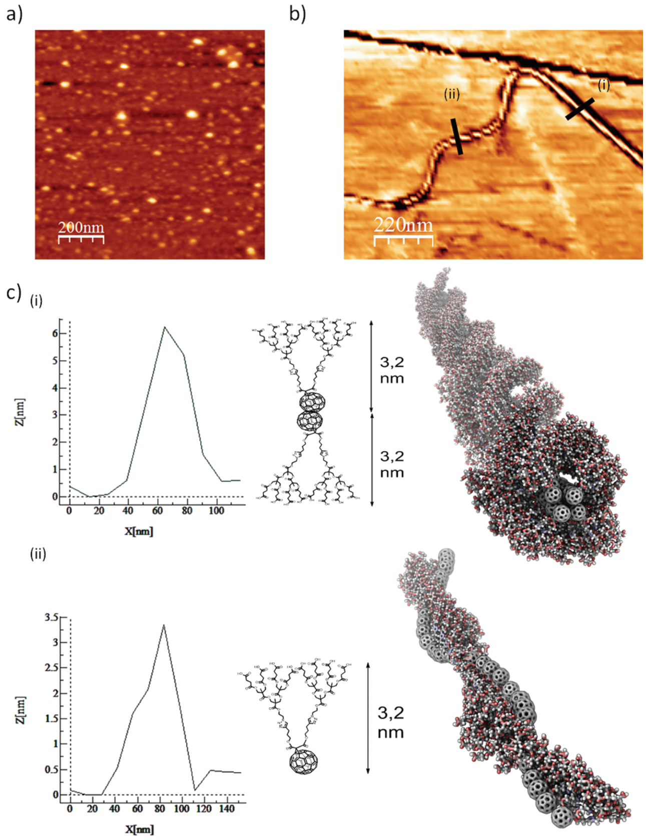

Figure 2. (a) Tapping mode AFM height image of aggregates formed in THF/H_2O 2/1 (1.2×10^{-5} M) after deposition of **DF-8** on mica; (b) phase images acquired by tapping-mode AFM of compound **DF-8** (1.2×10^{-5} M in THF/H_2O 2/1) deposited on HOPG; c) cross-sectional height profiles corresponding to (i) and (ii) marked in panel b.

of carboxylic groups (**3** and **4**, SI).[13] Under the CuAAC conditions, dendrimeric fullerene adducts **5**−**7** (SI) were obtained in good yields (72−84%).

Deprotection of acid groups was carried out by treating the TMS-protected derivatives **5**−**7** with trifluoroacetic acid under mild conditions, leading to the corresponding dendrofullerenes with 4, 8, or 16 acid groups (**DF-4**, **DF-8** and **DF-16**, respectively) in 94−95% yields.

These new derivatives were fully characterized by standard spectroscopic and analytical techniques (see the SI for full experimental details and characterization). Thus, the click reaction was easily confirmed by the presence of the signals characteristic of the 1,2,3-triazole units as a broad singlet around 7.6−8.2 ppm in the ^{1}H NMR spectra and the typical signals at $\delta \sim 124$ and 140−144 in the ^{13}C NMR spectra. Also, the disappearance of the alkyne signal in the IR spectra around 2100 cm^{-1} is evidence of the complete functionalization of the fullerene derivatives. Finally, MALDI-TOF spectra of all new compounds were in agreement with the proposed structures.

Aggregation behavior of new amphiphilic derivatives **DF-4**, **DF-8**, and **DF-16** was investigated by AFM, SEM, TEM, SAXS, and XRD. To study the aggregation structures by AFM, water was added to a solution of **DF** in THF (1.2×10^{-5} M) up to a proportion of THF/H_2O (v/v) 2/1. AFM for compound **DF-8** was carried out on mica and on highly oriented pyrolytic graphite (HOPG). When **DF-8** was deposited on mica, an extensive distribution of spherical aggregates was observed, with heights around 13−16 nm (Figure 2a). Taking into account that the estimated size of one molecule is ~3.2 nm, it seems that a small number of molecules are aggregated to form micelles. Interestingly, when we deposited the above-mentioned solution on HOPG, the formation of some nanorods with average diameters around 3.3 and 6.6 nm and several micrometers in length (Figure 2b,c and Figure S3) was observed. These aggregates clearly present a rope-like structure and the found diameters are in agreement with the dimensions calculated for one or two of these dendrofullerenes. In fact, it can be observed that nanowires formed by only one molecule merge to form the two-molecule height rods. The formation of these rods is probably made feasible by the better interaction of the hydrophobic part of the molecule, that is, the fullerene moiety, with HOPG.[14] We speculate that the more favorable interaction of the fullerenes with the surface, in first instance, and, second, H-bonding and van der Waals interactions between the dendrimeric moieties will favor the formation of the wires. AFM images obtained for **DF-4** and **DF-16** on HOPG exhibit only the formation of spherical aggregates of sizes from 6−8 nm to 30−35 nm, thus, corresponding to the aggregation of few molecules (Figure S1).

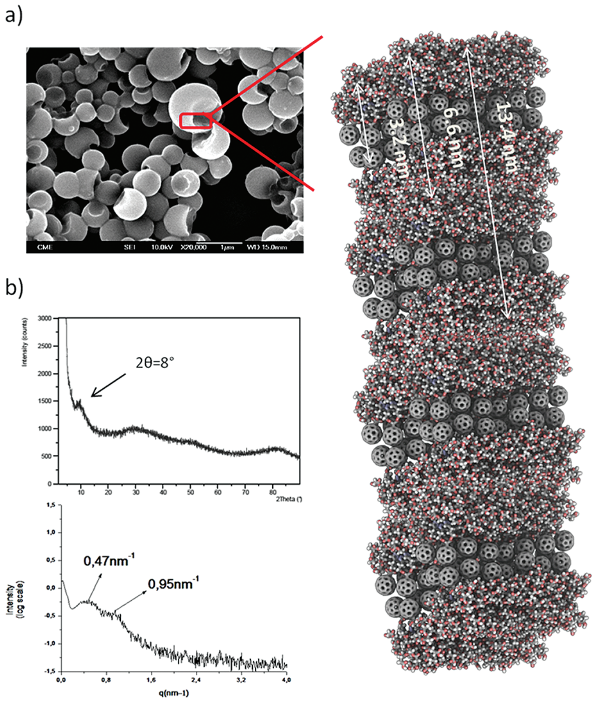

Figure 3. (a) SEM image (1.0×10^{-4} M in THF, glass substrate) of hollow vesicles formed from **DF-8**; (b) X-ray diffraction patterns at room temperature (top) and SAXS result for **DF-8** (THF, 1×10^{-4} M) (down).

Scanning electron microscopy (SEM) analysis of a solution of dendrofullerenes (10^{-4} M) in THF on glass substrate showed the formation of vesicles in the case of **DF-4** and **DF-8** (Figure 3a and Figure S4). It is interesting to note that the formation of these vesicles is more extensive for **DF-8** than for **DF-4**, while for **DF-16**, vesicles are not observed at all at this concentration (Figure S5). It could be explained by the bigger size of the hydrophilic part compared to the hydrophobic fullerene moiety in **DF-16**, which probably prevents the formation of the spherical aggregates observed in the less concentrated solutions to find a more favorable interaction between the molecules.

The observed vesicles are on average ∼400 nm in diameter. DLS experiments in solution (THF and THF/H_2O) have also demonstrated the formation of aggregates (Table S1). However, the analysis of these data has not allowed defining the particular morphology of the aggregates forming in solution. It should be reasonable to think that vesicles are also formed.

Analysis of **DF-4** and **DF-8** on carbon-coated grids by transmission electron microscopy (TEM) showed the formation of hollow vesicles with diameters varying from 200−300 nm to a few micrometers (Figure S8). Vesicles resulting from **DF-4** are bigger than those obtained from **DF-8**, probably as a consequence of a more expanded conical shape for the former.

To get a deeper understanding of the structure of these spherical particles, we characterized them by X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS). A sample prepared using the same method as in AFM and TEM analyses was employed for XRD characterization. The XRD pattern of **DF-8** showed a broad peak at $2\theta = 8°$, corresponding to a d spacing of ∼1 nm (Figure 3b and Figure S6). This distance fits well with the size of a molecule of fullerene, and therefore, it could be accounting for the disposition of fullerene molecules packed in contact with each other. This tight contact of the fullerene moieties in the vesicle membranes has been justified by the high cohesive forces between C_{60} molecules.[9c,15] In the corresponding intensity profile as a function of the scattering vector (q) obtained from SAXS (Figure 3b and Figure S7), we can see two scattering peaks at $q_1 = 0.47\ \text{nm}^{-1}$ and $q_2 = 0.95\ \text{nm}^{-1}$ which suggest a structure with a period of $d = 2\pi/q_{\max} = 13.4$ nm. This value is consistent with the size estimated for four molecules of **DF-8**. The q_2 value observed corresponds to a distance of 6.6 nm, which indicates the presence of two molecules of dendrofullerene. These data suggest that the shell of the vesicles is probably formed by a multilamellar packing of the molecules where the bilayers interact through H-bonding between polar carboxylic acid groups (Figure 3b).

In conclusion, we have described a very efficient procedure to obtain amphiphilic fullerene based molecules by using a click chemistry methodology. We have studied the aggregation behavior of these amphiphiles and found that the morphology of the supramolecular architectures formed varies depending on the surface and on the concentration of the samples analyzed.[16] This kind of aggregation could find applications on the design of new functional materials and in biological sciences. Work is currently in progress to determine the interest of these systems in the preparation of photovoltaic devices, where organization and morphology of the active materials at the nanometer scale is a key issue.[5d]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures and complete spectroscopic and structural characterization, including Figures S1−S8. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

nazmar@quim.ucm.es; javier.rojo@iiq.csic.es

■ ACKNOWLEDGMENT

Financial support by the MICINN of Spain (CTQ2008-00795/BQU, CTQ2008-01694), the CAM (MADRISOLAR-2 S2009/PPQ-1533), and Consolider-Ingenio CSD2007-00010, Nanociencia Molecular), and the EU (FUNMOL FP7-212942-1) is greatly appreciated. A.M. thanks the MICINN for an FPI Studentship. This Communication is dedicated to the memory of Prof. Rafael Suau.

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