Self-assembly of fullerene-rich nanostructures with a stannoxane core†

Uwe Hahn, Aline Gégout, Carine Duhayon, Yannick Coppel, Alix Saquet and Jean-François Nierengarten*

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Fullerene derivatives bearing a carboxylic acid function undergo self-assembly with *n*-butylstannonic acid (*n*BuSn(O)OH) to produce fullerene-rich nanostructures with a stannoxane core in almost quantitative yields.

Organooxotin cages have received considerable attention in view of their structural diversity.[1] Importantly, these compounds can be self-assembled in almost quantitative yields under very mild reaction conditions. Therefore, organotin chemistry appears to be an attractive tool for the preparation of multi-functional nanostructures. Indeed, Chandrasekhar and co-workers have already reported the self-assembly of a robust, thermally stable hexaferrocene assembly in quantitative yield by reaction of *n*-butylstannonic acid with ferrocene monocarboxylic acid.[2] By using a similar approach, the same group has also described the synthesis of a hexaporphyrin assembly with promising DNA cleavage activity.[3] In this paper, we now show that C_{60} derivatives bearing a carboxylic acid function undergo self-assembly with *n*-butylstannonic acid (*n*BuSn(O)OH) to produce fullerene-rich nanostructures with a stannoxane core in nearly quantitative yields. The preparation of fullerene-rich derivatives is indeed difficult and usually involves a high number of synthetic steps thus limiting their accessibility and therefore their applications.[4] The self-assembly of fullerene-containing components reported herein is an attractive alternative for their preparation. Indeed, fullerene-rich derivatives are thus easier to produce and the range of systems that can be prepared is not severely limited by the synthetic route. In this way, in-depth investigations of their properties is possible and one can really start to envisage the use of fullerene-rich materials for specific applications.

The starting carboxylic acid derivatives used in this study are depicted in Fig. 1. The reaction conditions for the self-assembly of the stannoxane derivatives were first adjusted with model compound **1a**. Under optimized conditions, a mixture of **1a** (1 equiv.) and *n*BuSn(O)OH (1 equiv.) in benzene was refluxed for 12 h using a Dean–Stark trap. After cooling, the solution was filtered and evaporated to dryness to afford the hexameric organostannoxane derivative **2a** in 99% yield. The drum-like structure of this compound made up of a prismatic Sn_6O_6 core was confirmed by its ^{119}Sn NMR spectrum recorded in C_6D_6 which shows a single resonance at −479.1 ppm (Fig. S1†). This chemical shift is characteristic of a drum-shaped structure with six equivalent Sn atoms coordinated by 5 oxygens and one carbon.[5]

Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of Et_2O into a C_6H_6 solution of **2a**.‡. Despite the disorder resulting from one of the flexible butyl chains, the central Sn_6O_6 stannoxane core and the six peripheral 2-phenoxyacetate units of the structure are well resolved. It can be noted that molecule **2a** lies about an inversion center in the solid state. As shown in Fig. 2, the prismatic tin cage is formed by two six-membered $(SnO)_3$ rings joint together by six Sn–O bonds.[6] The side faces of the cluster are thus comprised by six four-membered $(SnO)_2$ rings, each of which being spanned by a carboxylate group that forms a bridge between two Sn atoms. A detailed observation of the stannoxane framework reveals that the six-membered rings have a chair-like conformation. Each Sn atom is bonded to three framework oxygen atoms, where the Sn–O bonds have all comparable lengths ranging from 2.08 to 2.10 Å. The six Sn atoms are hexacoordinated, with the coordination sphere being completed by a *n*-butyl group and two oxygen atoms from two

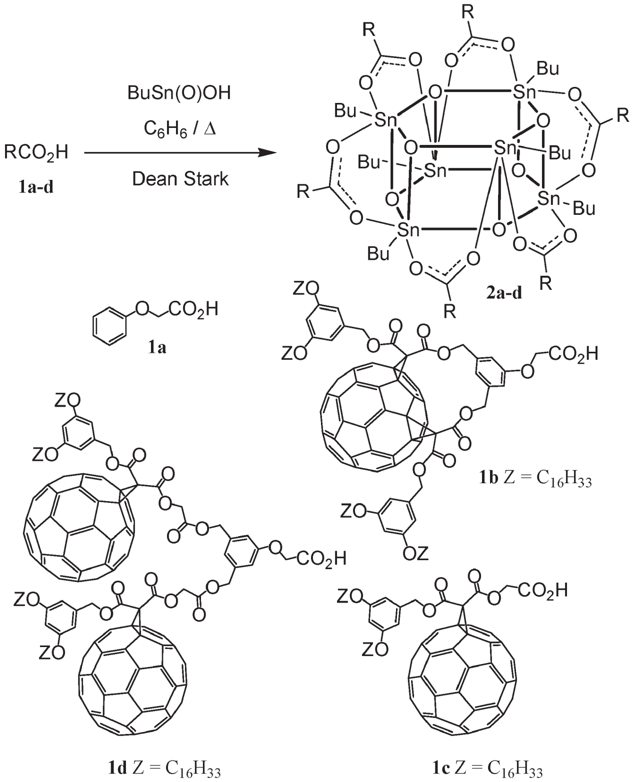

Fig. 1 Preparation of compounds **2a–d** from the corresponding carboxylic acid derivatives **1a–d**.

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077, Toulouse Cedex 4, France.
E-mail: jfnierengarten@lcc-toulouse.fr; Fax: +33 (0) 5 61 55 30 03; Tel: +33 (0) 5 61 33 31 51

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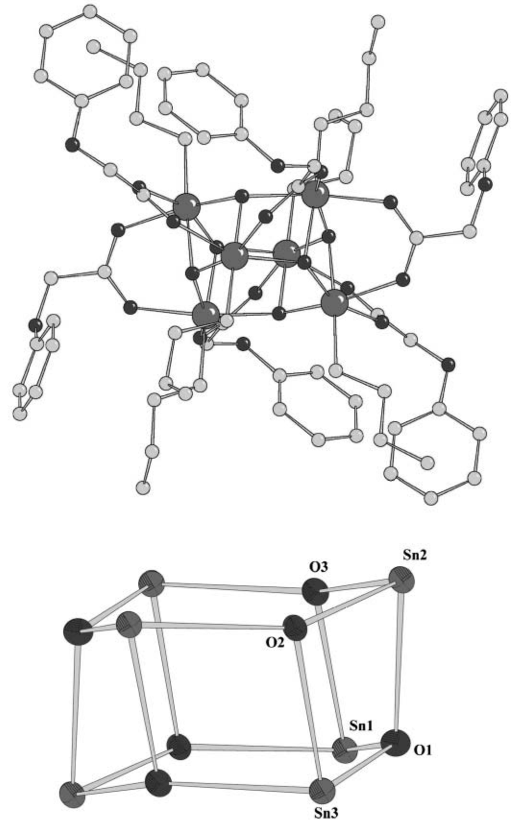
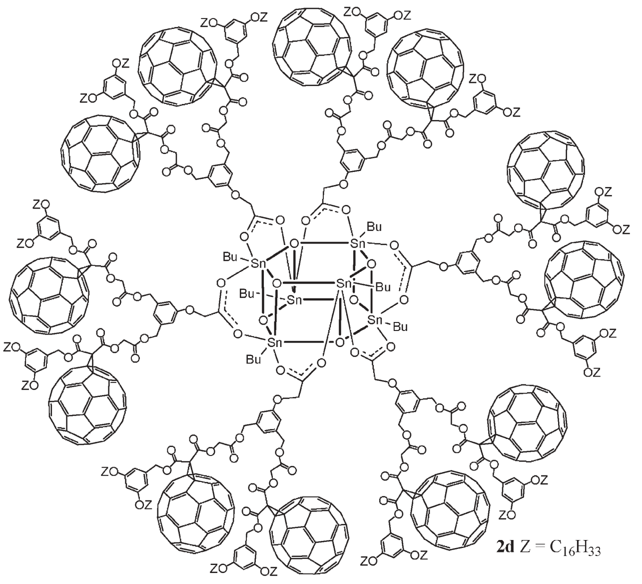


Fig. 2 Top: X-ray crystal structure of **2a** (C: pale gray, O: black, Sn: gray); Bottom: detailed view of the Sn_6O_6 core. Selected bond lengths: Sn(1)–O(1): 2.084(3) Å, Sn(2)–O(1): 2.075(4) Å, Sn(2)–O(2): 2.097(3), Sn(2)–O(3): 2.093(3) Å, Sn(3)–O(1): 2.101(3) Å.

different carboxylate groups. The Sn–O bonds to the bridging carboxylate atoms are longer than the core bonds and range from 2.15 to 2.18 Å.

The reaction conditions used for the preparation of **2a** from 2-phenoxyacetic acid were applied to the fullerene building blocks **1b–d**.[7] The organostannoxane derivatives **2b–d** were thus obtained in almost quantitative yields. The largest assembly is represented bellow.

These compounds are well soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, C_6H_6 or toluene and complete spectroscopic characterization was easily achieved. The ^1H and ^{13}C NMR spectra of **2b–d** clearly reveal the characteristic signals of the starting carboxylic acid precursors **1b–d** as well as the expected additional resonances arising from the *n*-butyl chains. Importantly, the spectra clearly showed that all the peripheral fullerene subunits are equivalent in **2b–d** as expected for a six-fold symmetric assembly with a drum-shaped organostannoxane core. As depicted in Fig. 3, a single resonance is observed at *ca.* −480 ppm in the ^{119}Sn NMR spectra of **2b–d** recorded in C_6D_6. This characteristic signature of tin-drum clusters provides definitive evidence for the formation of **2b–d**. It can be added that a significant broadening is observed in the ^{119}Sn NMR spectra obtained from **2b–d** when compared to the one recorded for **2a** under the same conditions. The latter observation is indeed ascribed to significant changes in the relaxation time T2 as a result of the large increase in molecular weight.



2d Z = $C_{16}H_{33}$

The absorption spectra obtained from CH_2Cl_2 solutions of compounds **2b–d** are identical to the ones recorded for the corresponding starting carboxylic acid precursors thus showing the absence of significant influence of the stannoxane core on the electronic properties of the fullerene moieties. To further confirm that the characteristics of the fullerene subunits are maintained for **2b–d**, their electrochemical properties were investigated by cyclic voltammetry (CV). For the sake of comparison, electrochemical measurements have also been carried out with **2a** and the *t*-butyl esters **1b**-^{t}Bu and **1c**-^{t}Bu derived from **1b** and **1c**, respectively. All

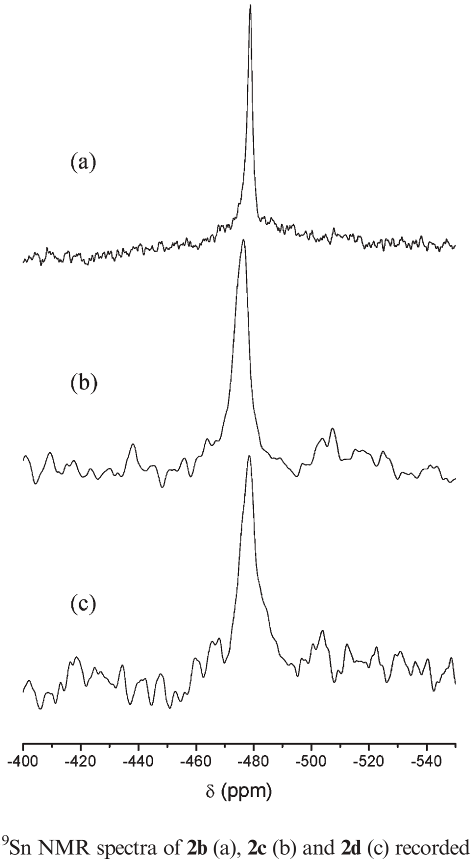


Fig. 3 ^{119}Sn NMR spectra of **2b** (a), **2c** (b) and **2d** (c) recorded in C_6D_6.

Table 1 Electrochemical data on the reduction of **2b–d**, **1b**-^{t}Bu and **1c**-^{t}Bu determined by CV on a Pt working electrode in CH_2Cl_2 + 0.1 M ^{n}Bu$_4$NBF$_4$ at room temperature[a]

	E_1	E_2	E_3
1b-^{t}Bu	−0.59 (70)	−0.91[b]	−1.23[c]
2b	−0.60 (70)	−0.92[b]	−1.22[c]
1c-^{t}Bu	−0.51 (75)	−0.89 (75)	−1.34 (65)
2c	−0.53 (85)	−0.91 (80)	−1.35 (110)
2d	−0.54 (75)	−0.92 (90)	−1.33 (110)

[a] Values for $(E_{pa} + E_{pc})/2$ in V *vs.* SCE and ΔE_{pc} in mV (in parenthesis) at a scan rate of 0.1 Vs^{-1}. [b] Irreversible process, peak potential measured at 0.1 Vs^{-1}. [c] Small amplitude wave corresponding to an electrogenerated species obtained after the second reduction step.

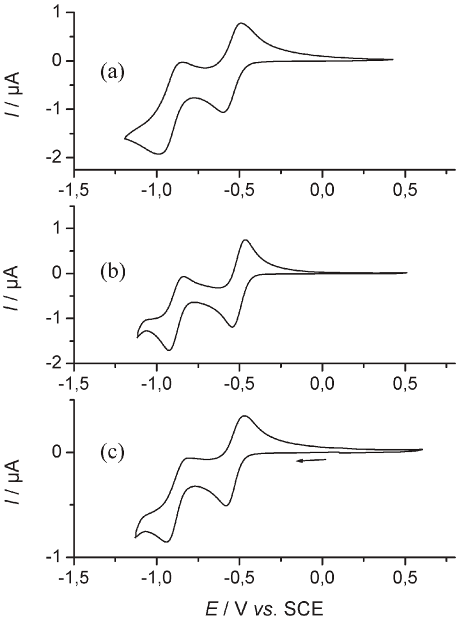


Fig. 4 Cyclic voltammograms showing the two first reductions of **2c** (a), **1c**-^{t}Bu (b) and **2d** (c) on a Pt electrode at v = 0.1 Vs^{-1} in CH_2Cl_2 + 0.1 M ^{n}Bu$_4$NBF$_4$.

the experiments were performed at room temperature in CH_2Cl_2 solutions containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as supporting electrolyte, with a Pt wire as the working electrode and a saturated calomel electrode (SCE) as a reference. Potential data for all of the compounds are collected in Table 1. As typical examples, the cyclic voltammograms obtained from **2c–d** and **1c**-^{t}Bu are shown in Fig. 4.

In the anodic region, all the studied compounds present at least one irreversible peak at *ca.* +1.7–1.9 V *vs.* SCE than can be likely attributed to the oxidation of the dialkyloxyphenyl and/or alkyloxyphenyl units.[8] Whereas model compound **2a** was found to be electrochemically silent in the cathodic region, the fullerene-substituted stannoxane derivatives **2b–d** revealed the typical electrochemical response of fullerene derivatives.[9] Compound **2b** shows the characteristic behavior previously reported for fullerene *cis*-2 bis-adducts.[10] Whereas the first reduction, which occurs at −0.60 V *vs.* SCE, is reversible, the second reduction observed at *ca.* −0.9 V is irreversible. It has actually been shown that the second electron transfer in *cis*-2 derivatives is followed by a chemical reaction leading to an undefined electrogenerated species that is reduced at −1.2 V.[10] Comparison with the results obtained with model compound **1b**-^{t}Bu reveals no significant differences and shows that all the six peripheral fullerene subunits of **2b** behave as independent redox centers. The model compound **1c**-^{t}Bu presents the characteristic features of methanofullerenes[11] and several reduction steps are observed. The electrochemical behavior of **2c** and **2d** appears to be similar to that of the model compound **1c**-^{t}Bu. This indicates that all the methanofullerene moieties in **2c–d** behave as independent redox centers and that their electrochemical properties are not affected by the stannoxane core.

In conclusion, we have reported a very efficient procedure for the self-assembly of fullerene-rich nanostructures. As the electronic properties of the parent fullerene derivatives are maintained in these supramolecular ensembles, they appear as potentially interesting accepting materials for the preparation of solar cells.[12] In this view, their high molecular weight associated to a high fullerene content are clear advantages.

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Notes and references

‡ $C_{72}H_{96}O_{24}Sn_6$ (M_r = 2057.68), triclinic space group *P*-1, Z = 1, *a* = 10.485(5), *b* = 14.553(5), *c* = 14.702(5) Å, *α* = 70.400(5), *β* = 70.773(5), *γ* = 72.287(5)°, *V* = 1947.6(13) Å^3.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614009b

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