Experimental report

26/06/2019

Proposal: **9-13-713**

Council: 4/2017

Title: Investigation of a fullerene basedphytochemical supramolecular complex with proven biomedical activity

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
H_2O
D_2O
fullerene, C_{60}
Dihydroquercetin, $C_{15}H_{12}O_7$

Instrument	Requested days	Allocated days	From	To
IN4	4	4	29/03/2018	02/04/2018
IN1	2	2	22/06/2018	24/06/2018
D16	3	3	26/03/2018	29/03/2018

Abstract:

Date of report **June 2019.**

The aim of the work was to evaluate the molecular structure of the synthesized water-soluble complexes of the dihydroquercetin (DHQ) enhanced by nanomaterials, such as fullerene (C_{60}) and fullerenol ($C_{60}(OH)_{24}$) to reveal the interaction formed between the nanocarbon and the phytochemicals, to verify the structure, molar ratio either C_{60} or $C_{60}(OH)_{24}$ and DHQ in their complex and to evaluate role of the structural water/hydrated shell there.

From the **proposed experiments** combined **SANS-diffraction** study was performed for the following supramolecular complexes [C_{60}-DHQ] and [$C_{60}(OH)_{24}$-DHQ]. At the beginning of the experiment a detailed contrast matching study was performed aimed at determining exact solvent composition for the match point of the fullerene/fullerenol. The SANS-diffraction measurement on **D16**, was done at 0.02-2 Å-1 range. All the measurements were performed at room temperature.
The structural study was complemented by neutron spectroscopy measurements on **IN4 and IN1-Lagrange**. On IN1-LAGRANGE, the C_{60} vibrations was studied in their complete 30-200 meV range. The fullerene vibrations are sensitive both to their direct environment and to the nature of the interaction with the DHQ: any strong coupling (covalent bridges) was significantly perturb the C_{60} shape resulting in a very different spectral signature, while any charge transfer from the C_{60} to the surrounding molecule affected the position and width on some specific modes of the spectrum. In the external mode range (IN4C instrument) the dynamics of the encaged C_{60} molecule was probed. The specific vibration (hindered rotations) and translational modes patterns was used to derive information on the local symmetry and curvature of the potential energy surface. These features gave precise information on the interactions at state in this system. The experiments for all samples were done in two different states of aggregation, one in the solid state and one in liquid (dissolved in D_2O) states. The dissolved sample was quenched down to low temperature. On IN4 as well as on IN1-LAGRANGE, two incident wavelengths were used (1.1 and 2.2 Å).

Results & Discussion

D16 data analysis:

The red curve shows the characteristic Bragg peaks of C_{60}. In the green curve [C_{60}-DHQ] a different crystalline structure is observed. The Bragg peaks of C_{60} are not fully recognizable, it is suspected that almost all peaks are coming from the DHQ. The compounds are crystalline.

The blue curve shows the signal of the [$C_{60}(OH)_{24}$-DHQ]. The total absence of Bragg peaks shows that the compound is not crystalline, but in an amorphous form. There is one broad peak at around Q=0.068 Å^{-1}, which corresponds to a distance of $d=2\pi/Q=92$ Å. This is an indication of an ordering in the sample at this lengths scale.

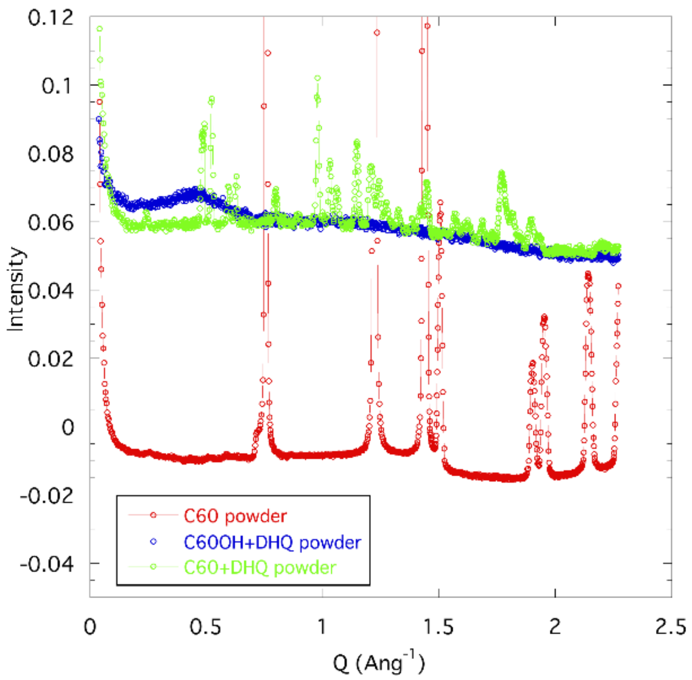

Figure 1. Small/wide angle neutron scattering data on powders obtained on D16.

IN4C & IN1-LAGRANGE data analysis:

Based on the data obtained in was established the core of the supramolecular complexes [C_{60}-DHQ] and [$C_{60}(OH)_{24}$-DHQ].

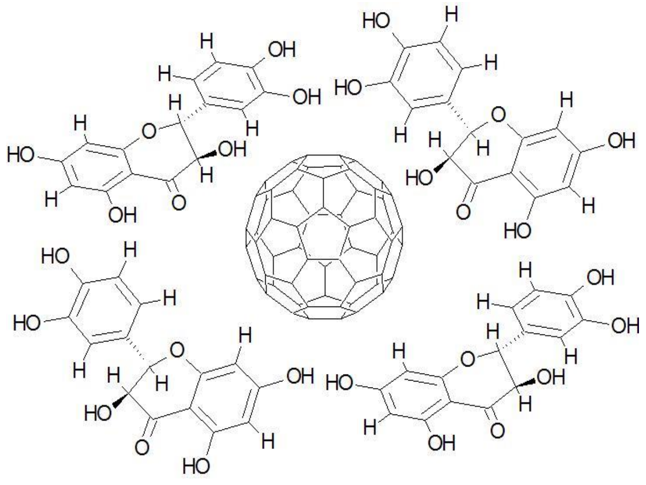

Figure 2. COMPLEX of 1C60 surrounded by 4 DHQ. The proven structure of the core of the complex

It was proven, that water –soluble [C_{60}-DHQ] and [$C_{60}(OH)_{24}$-DHQ] supramolecular complexs is formed with molar ration of the components:

[1C_{60} to 4DHQ]
[1 $C_{60}(OH)_{24}$-to 6 DHQ],

where Donor (DHQ) –Acceptor (C_{60} or $C_{60}(OH)_{24}$) type of bindings and Van der Waals interactions between C_{60} or $C_{60}(OH)_{24}$ host and DHQ guest play an important role, resulting in the highly stable complex.

There were also evidence that the complex surrounded by water molecules generating the clusters of the complex with water. Furthermore, such the clusters could be further aggregated by aqueous clusters.

The recalculation (quantification data evaluation) and reconstruction of the structure of the surrounded hydrated shell and amount of the water molecules there is under the progress.

First set of data analysis, based on the modeling of the experimental data, is presented in Fig. 3.

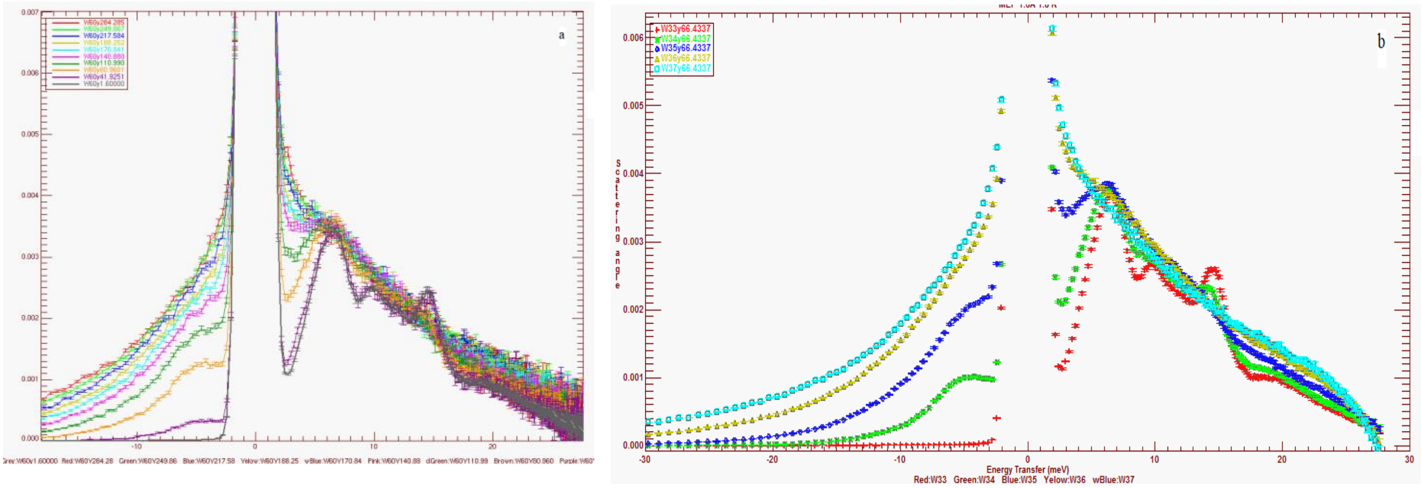

Figure 3. First set of data analysis of the IN4 experimental data for individual components C_{60}, $C_{60}(OH)_{24}$, DHQ and their water-soluble complexes.