

**FINAL PROJECT REPORT FOR EUROPEAN SCIENCE  
FOUNDATION PROGRAMME (ORGANISOLAR)**

**NOVEL [60]FULLERENE BASED MATERIALS FOR THE  
PREPARATION OF PHOTOVOLTAIC DEVICES**

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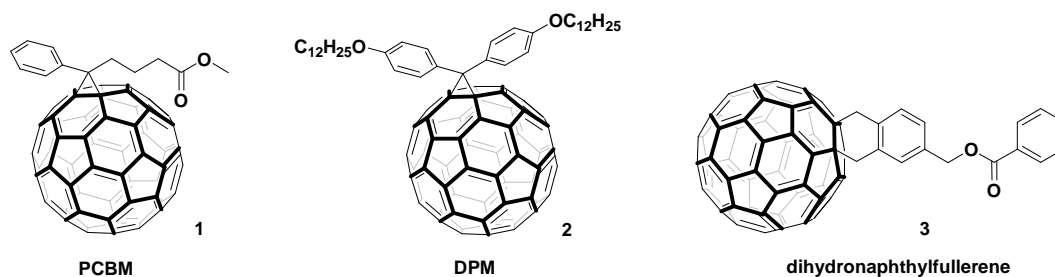
## **AIM of VISIT**

**Fullerene molecules are important molecular structures for the development of photovoltaic device technology. I have learned Fullerene chemistry thanks to this visit. Prof. Dr. Nazario Martin Leon has more experience on the topic of both fullerene chemistry and photovoltaics.**

### **1. Introduction**

Global dependence on fossil fuels is a key issue with important consequences in the world nowadays.<sup>i</sup> A reasonable solution to overcome this need is the use of renewable energy sources,<sup>ii</sup> like solar energy, that could in principle, fulfill our energy requirements with clean procedures and low prices. In this context, the preparation of photovoltaic devices based on organic materials, suitable to convert solar energy into electrical power is a challenging research field for many scientists around the world. Fullerene and fullerene derivatives possess important properties like small reorganization energy, high electron affinity, ability to transport charge and stability, that makes them the best candidates to act as electron acceptors in bulk heterojunction (BHJ) photovoltaic (PV) devices, mixed with conjugated polymers like P3HT or MDMO-PPV.<sup>iii,iv</sup> To date, PCBM ([6,6]-phenyl C<sub>61</sub> butyric acid methyl ester) (**1**) first obtained by Hummelen and Wudl in 1995,<sup>v</sup> remains the most common fullerene derivative employed for the preparation of PV devices and solar cells based on this material displaying reproducible efficiencies approaching 5%.<sup>vi</sup> BHJ-PV devices based on further methano[60]fullerene materials like DPM (**2**) have shown as well, efficient and promising conversion of solar energy.<sup>vii</sup> In addition to methano[60]fullerene based materials, other fullerene derivatives have been synthesized and used in the preparation of BHJ-PV devices,<sup>viii</sup>

however, up to now, only materials based on the dihydronaphthylfullerene skeleton (**3**) have been reported to give similar performances (4.5%) to that of PCBM.<sup>ix</sup>



**Figure 1:** Fullerene-based materials employed as acceptors in BHJ-PV devices.

Among other parameters, the ability of both the conjugated polymer and the fullerene derivative to collect energy from the sunlight is essential to warrant nice performance of the PV device. [60] Fullerene derivatives display low absorption in the visible range, due to the high degree of symmetry of this fullerene,<sup>x</sup> limiting therefore the capability to harvest energy of the final BHJ-PV device.

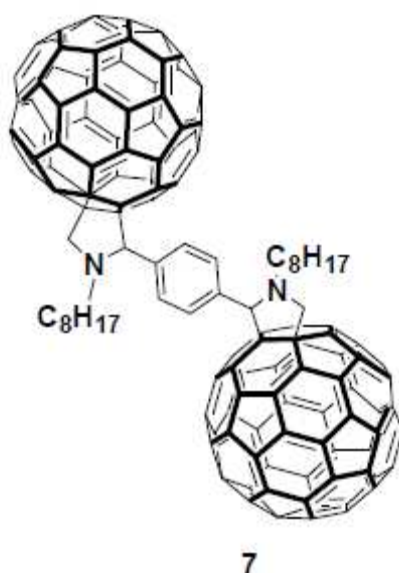
Stimulated by an idea to combine good electron accepting and light harvesting properties, we introduced recently a new class of fullerene-based materials, constituted by two covalently connected fullerene units (C<sub>60</sub> and/or C<sub>70</sub>).<sup>xi</sup> The resulting dimers endowed with a solubilizing alkyl chain exhibit increased light-harvesting properties, due to the presence of two units of identical (**1,2**) or different (**3**) fullerenes linked through a 2-pyrazoline and a pyrrolidine rings (Figure 1). Photovoltaics devices were prepared with blends of these materials and P3HT and according to our expectations, the P3HT:**3** based solar cell exhibited the most promising external quantum and power conversion efficiencies being as high as 37% and 0.91%, respectively.

Tetrathiafulvalenes with extended  $\pi$ -conjugation (exTTF) are a well-known class of electron donor system (Figure 3).<sup>12</sup> Here we investigate the photovoltaic potential of sensitizers with a tetrathiafulvalene derivative donor and a cyanoacrylic acid acceptor in

DSCs. The out-of-plane butterfly shape of the exTTF provides steric hindrance,<sup>13</sup> preventing self-aggregation of the sensitizer, a significant parameter in the performance of DSCs.

## 2. Results and Discussion

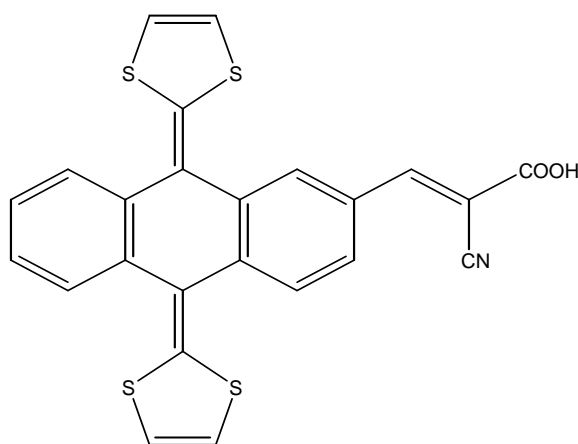
We have decided to explore this field and synthesize a new family of fullerene dimers where the LUMO level will be energetically higher. As a consequence we expect to increase the open circuit voltage in devices of these materials (**7**) blended with P3HT, and therefore the power conversion efficiency (PCE). Moreover, we expect to improve the processability of these materials, facilitating therefore its incorporation in PV devices. (Figure 2)



**Figure 2**

In order to increase the solubility and processability of the fullerene dimers, different alkyl chains have been synthesized, to study the influence of the solubilizing group, over the efficiency of the device. Also, chemically modified tetrathiafulvalenes were synthesized in order to study its potential application in the preparation of DSSC.

All these systems were fully characterized using the spectroscopic available techniques (NMR, MS, HPLC), and prepared in appropriate amount in order to facilitate its photophysical and photovoltaic study. Mass analysis showed the expected molecular ion peaks of the fullerene dimers, confirming therefore the formation of these systems. Also we prove the purity with HPLC for all the materials after classical column chromatography and GPC.



**Figure 3** Molecular structure of functionalized ex TTF sensitizer

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