

# Scientific Report

on the

## Exchange Grant

*“Material structure-solubility-photovoltaic performance relationships for composites of poly(3-alkylthiophenes) with various fullerene derivatives”*

within the **ORGANISOLAR**-Program  
of the European Science Foundation

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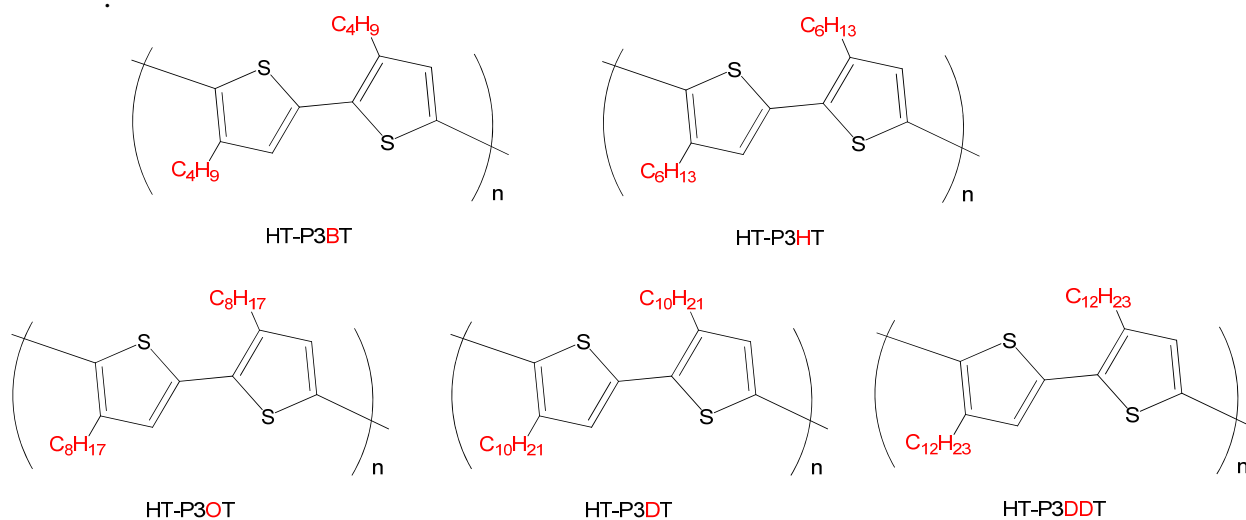
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# 1. Purpose of the visit

We have shown recently that all parameters of the poly(3-hexylthiophene)-based bulk heterojunction organic solar cells depend strongly on the solubility of the fullerene derivative used as electron acceptor component [1-2]. Such dependence is related to the influence of the relative material solubility on the photoactive blend morphology. For instance, increase in the solubility of the fullerene component by a factor of 2 decreases degree of the phase separation in the blend with P3HT (size of separate clusters) by a factor of 10. On the basis of the obtained results it can be easily concluded that material solubility is one of the most important issues that should be considered in the development of improved organic photovoltaics.

In the frame of the present project we plan to investigate a wider range of poly(3-alkylthiophenes) with butyl, hexyl (combined with some new fullerene derivatives), octyl, decyl and dodecyl side chains (Figure 1) in combination with fullerene derivatives possessing different solubilities in organic solvents (structures not shown). This work should reveal some correlations between the molecular structures of the materials, their physical properties, morphology of their blends and their photovoltaic performances.



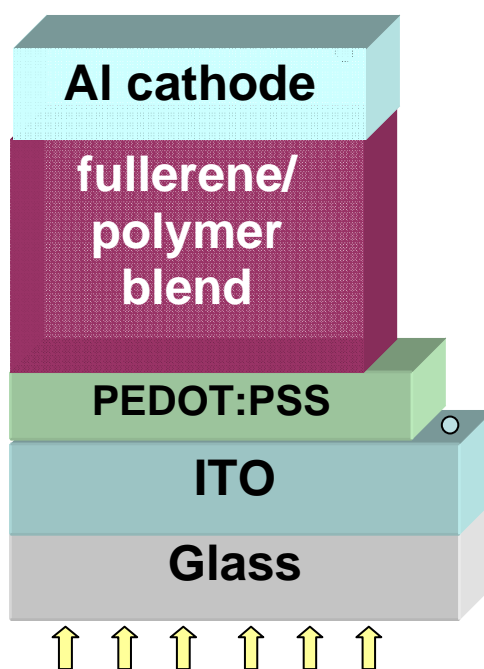
**Figure 1 Molecular structures of the electron donor poly(3-alkylthiophenes) that will be investigated**

## 2. Description of the work carried out during the visit

We synthesized at home Institution a large range of fullerene derivatives possessing different molecular structures and different physical properties, particularly solubility. We selected 13 such fullerene derivatives and combined them with 5 different conjugated polymers: poly(3-butylthiophene) **P3BT**, poly(3-hexylthiophene) **P3HT**, poly(3-octylthiophene) **P3OT**,

poly(3-decylthiophene) **P3DT** and poly(3-dodecylthiophene) **P3DDT**. Molecular structures of polymers are shown in Figure 1. Molecular structures of fullerene derivatives used in this study we cannot disclose in this report because now we are preparing a publication on the base of the obtained results.

Thus, combination of 13 different fullerene derivatives with 5 polymers yielded 65 composite systems that we investigated as active layer materials in bulk heterojunction organic solar cells. The layout of such cell is shown in Figure 2.



**Figure 2** Layout of the investigated bulk heterojunction organic solar cell

We fabricated approximately 800 photovoltaic devices and characterized them by standard dark and light-on I-V measurements. Additionally we measured approximately 200 Atom Force Microscopy (AFM) and optical microscopy images in order to reveal topology of the prepared composite films. The obtained extensive set of the numerical and graphical data was treated using Origin, Excel and specialized n-Surf software.

The performed analysis of the data addressed the following major issues:

- Influence of molecular structures of donor polymers on the morphology of their composites with fullerene derivatives and on their performance in solar cells. We expect that some solar cell output parameters can be correlated with the length of alkyl side chains incorporated in the molecular structures of poly(3-alkylthiophenes) used as electron donor materials in the photoactive layers.

- Influence of the material solubility on the morphology of the blends and on their photovoltaic performance.
- Influence of the molecular structures of fullerene derivatives on the morphology of their composites with poly(3-alkylthiophenes) and on their performance in solar cells.

The obtained results are presented below.

### 3. Description of the main results obtained

#### 3.1 Effect of the polymer structure on the solar cell performance

*It was revealed that length of the alkyl side chain attached to the polymer backbone dramatically effects solar cell performance.*

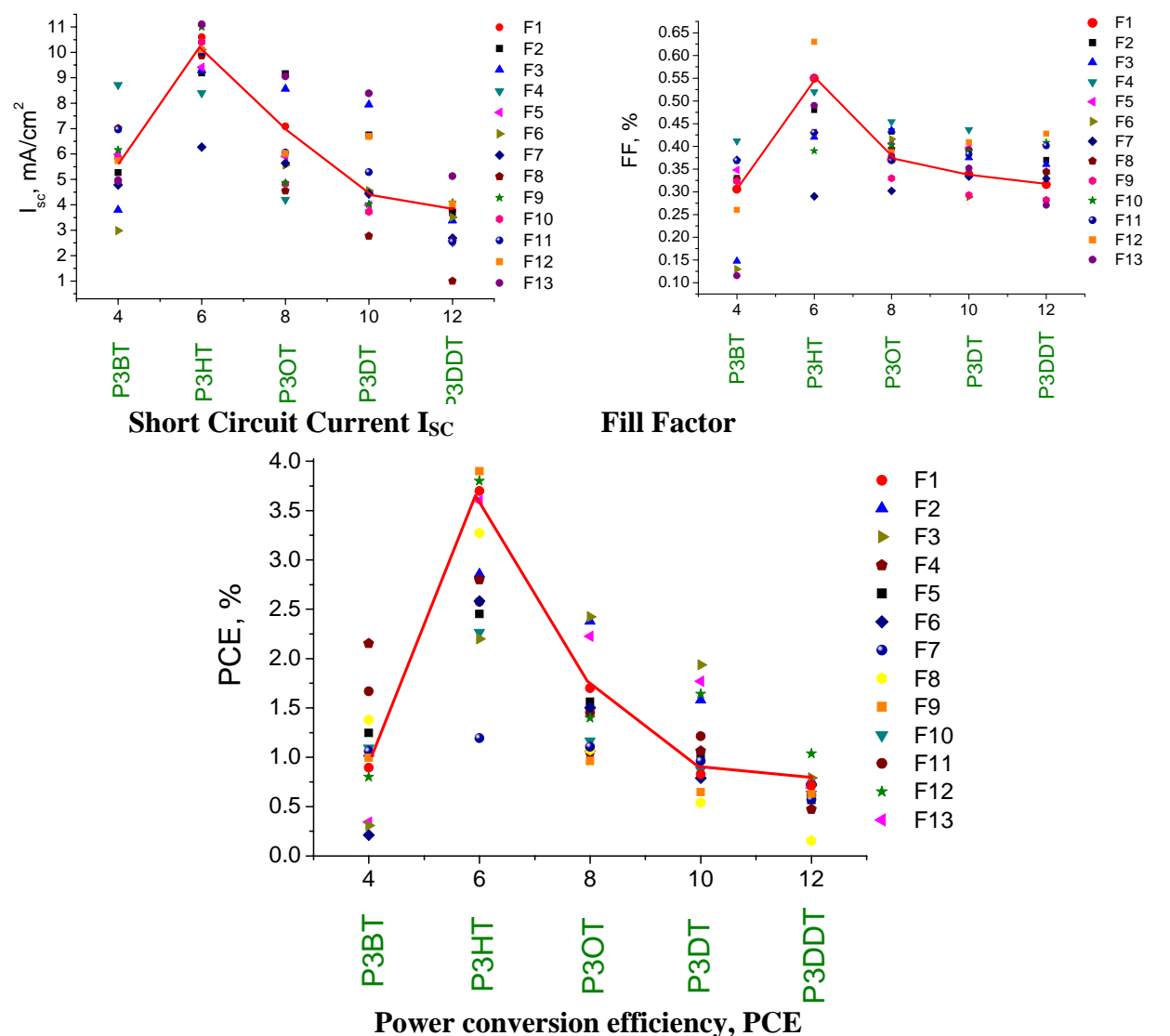
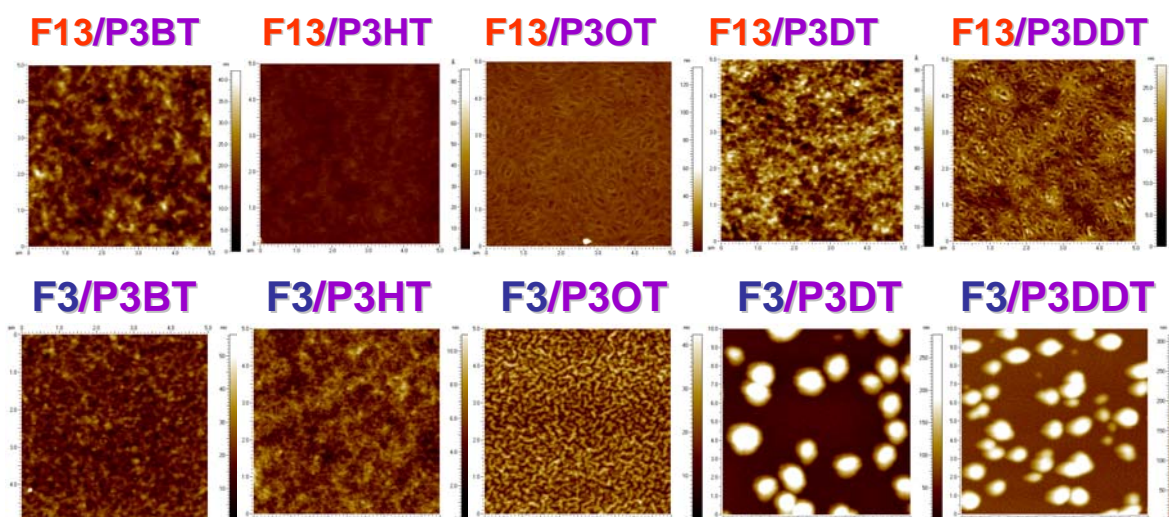


Figure 3 Dependence of the solar cell output parameters on the molecular structure of the used donor polymer. F1-F13 denotes investigated fullerene derivatives

All 13 investigated fullerene derivatives yielded the best results in solar cells when combined with **P3HT** as donor polymer. We note here that it was shown before that fullerene derivative PCBM works better in blends with P3HT than with other poly(3-alkylthiophenes) [3]. Here we showed that this is a general trend valid for all fullerene derivatives. Figure 3 shows that short circuit current, fill factor and power conversion efficiency change significantly going from one polymer to another. No such clear correlation was observed for open circuit voltage (plot not shown) because it is determined mostly by energy levels of the materials that were set more or less equal among the groups of acceptor (fullerenes) and donor (polymers) compounds. The observed effects are related most probably to the active layer morphology which is significantly influenced by the alkyl side chains attached to the polymer backbone. The change of the active layer morphology induced by the polymer side chains is illustrated for fullerene derivatives **F3** and **F13** in Figure 4.



**Figure 4** The change of the active layer morphology induced by the polymer side chains in composites of two fullerene derivatives with poly(3-alkylthiophenes)

### 3.2 Effect of the solubility of the fullerene component on the solar cell performance

We investigated previously composites of P3HT with various fullerene derivatives (27 compounds) [1]. We showed that there is a remarkable dependence of the solar cell output parameters on the solubility of the fullerene derivatives applied as acceptor components in the device active layers. This dependence has maximum which defines optimal solubility of the

fullerene derivative that is required for high performance. These dependences are illustrated in Figure 5.

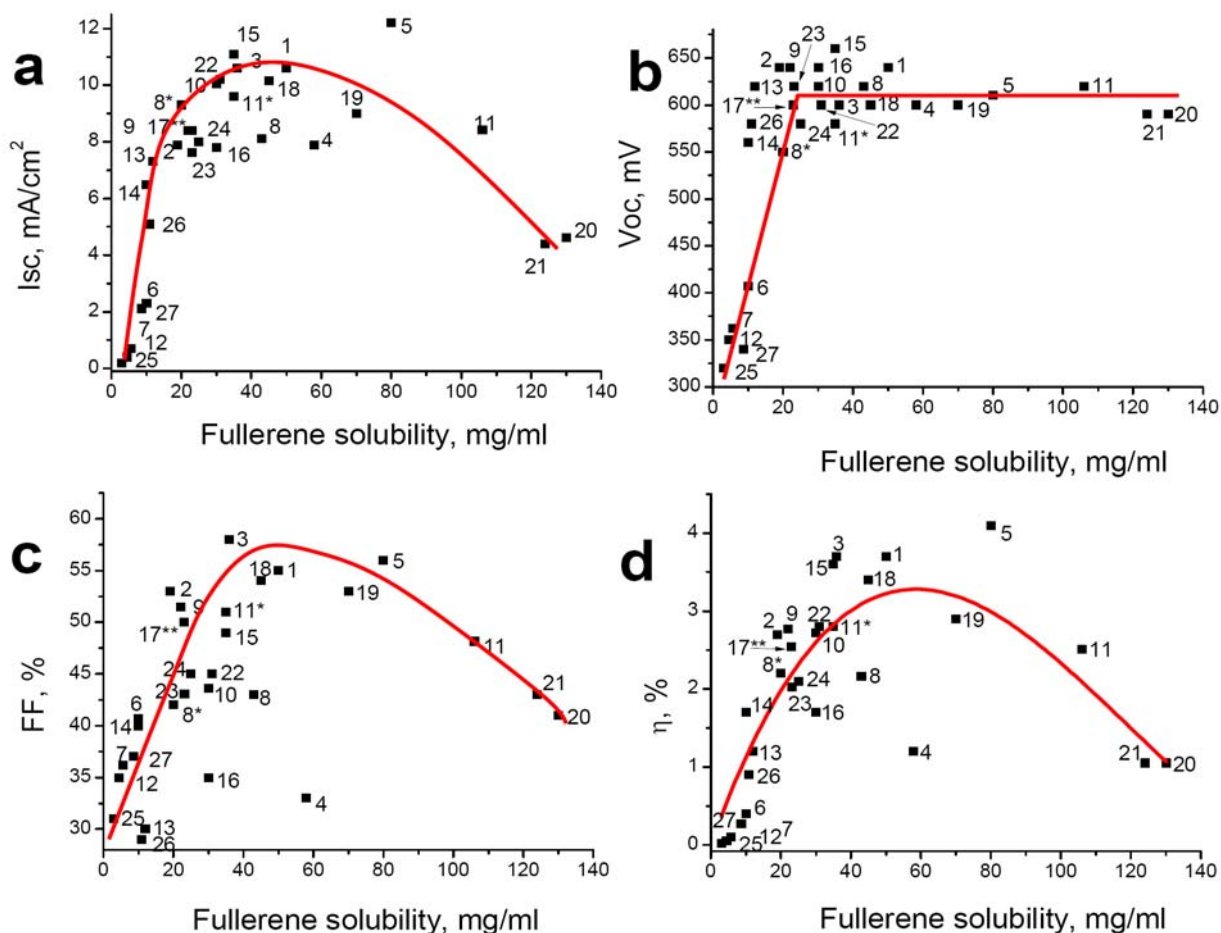


Figure 5 Dependence of the solar cell parameters on the solubility of the applied fullerene-based material. Each point on the plot denotes specific fullerene derivative. Solubilities were measured in chlorobenzene which was used as solvent for active layer deposition. Reproduces with permission from [1].

We expected to observe similar solubility dependences for all other investigated poly(3-alkylthiophenes). However, experimental study provided different results. To our great surprise, two investigated polymers (**P3OT** and **P3DT**) revealed very unusual double-branch type solubility dependences shown in Figure 6. These results were fully reproducible thus indicating that the observed double branch behavior cannot be an experimental error.

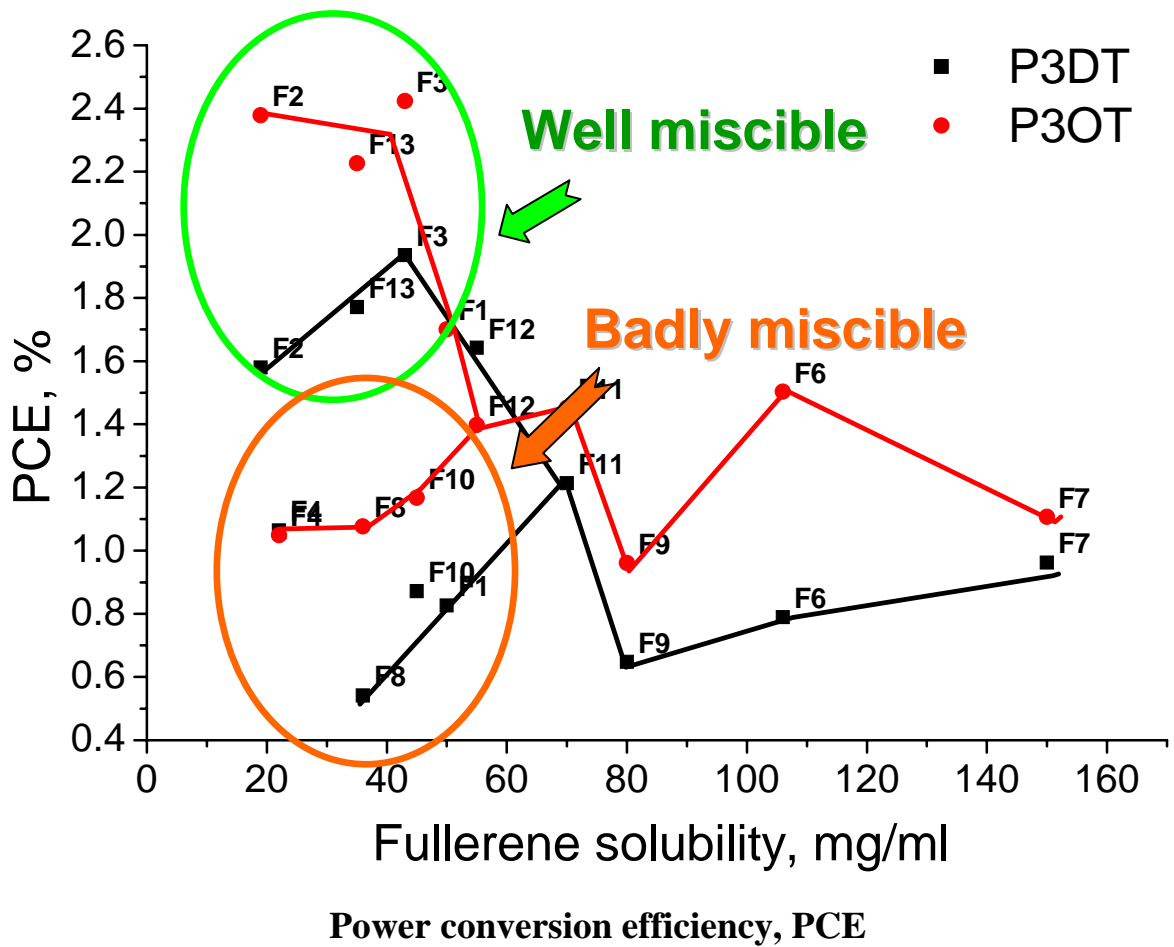
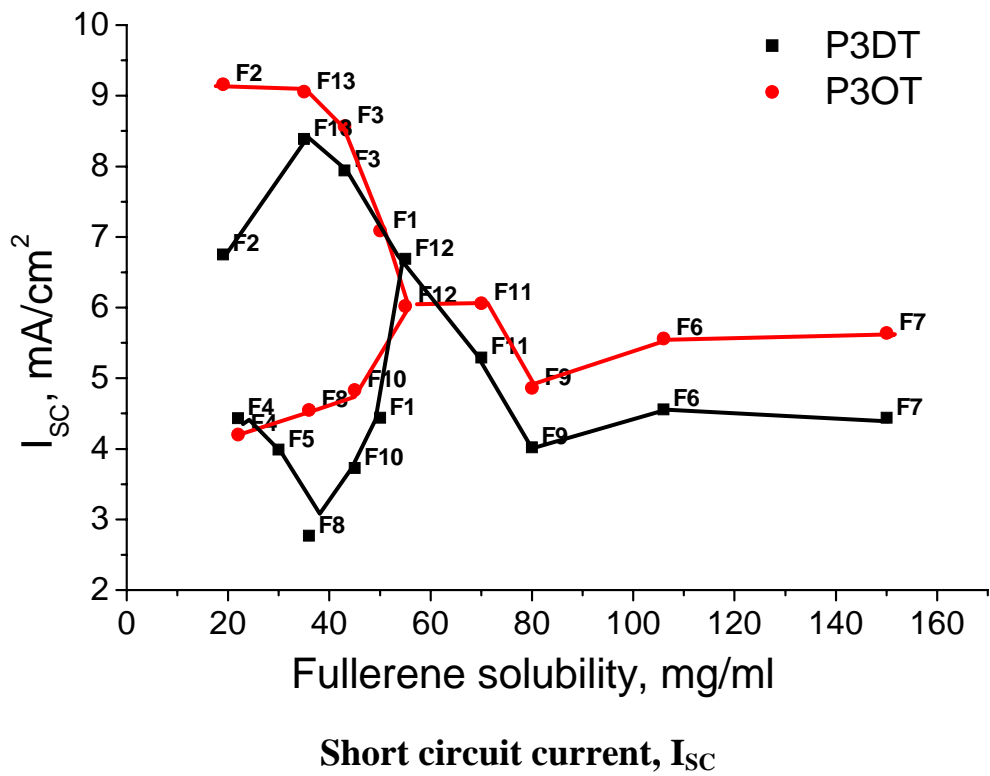


Figure 6 Solar cells output parameters as a function of the solubility of the fullerene-based materials used as electron acceptor components in blends with **P3OT** and **P3DT**.



### 3.3 Effect of molecular structure of the fullerene derivatives on the solar cell performance

In order to understand the observed double-branch type solubility behavior of organic solar cells comprising P3OT and P3DT, we performed AFM studies for all prepared fullerene/polymer composites. Indeed, AFM studies showed that blend morphology depends on the molecular structures of the fullerene derivatives.

Thus, example 1 shown in Figure 7 illustrates that two compounds (**A** and **B**) with very similar solubilities and different molecular structures give sharply different blend morphologies with P3DT. At the same time, example 2 shows that compounds **C** and **D** possessing similar molecular structures give similar blend topologies with P3OT regardless large difference in their solubilities.

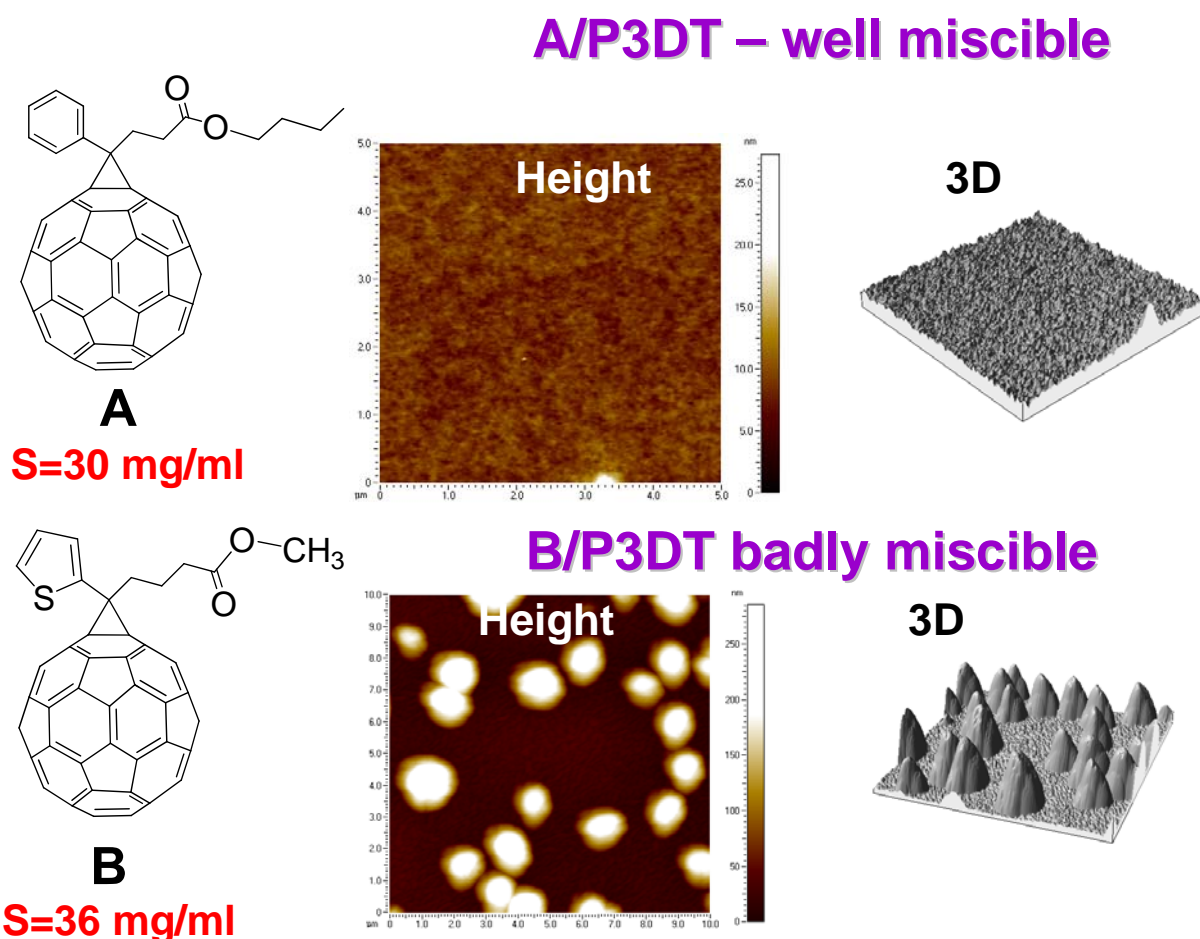
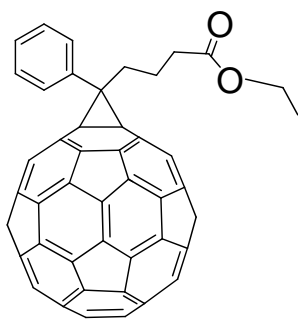


Figure 7 **Example 1** showing that fullerene derivatives with similar solubilities might give different very film topologies in blends with P3DT

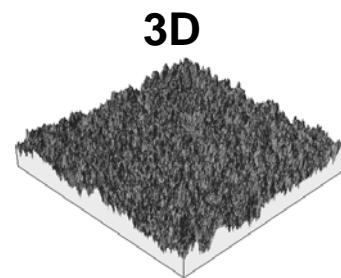
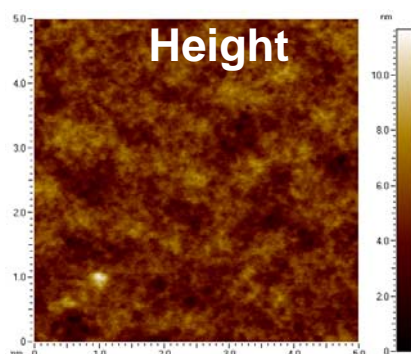


## C/P3OT – well miscible

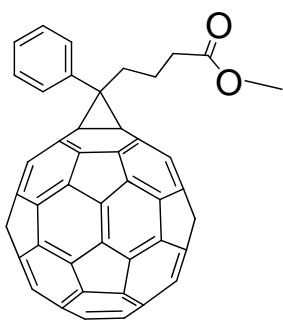


**C**

**S=19 mg/ml**



## D/P3OT-well miscible



**D**

**S=50 mg/ml**

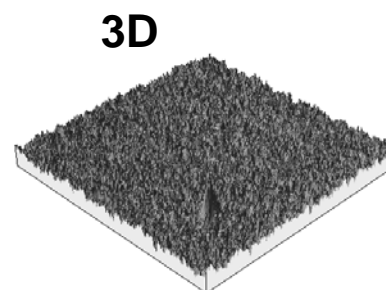
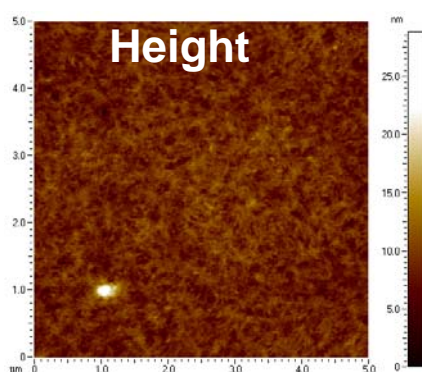


Figure 8 **Example 2** showing that compounds **C** and **D** possessing similar molecular structures give similar blend topologies with **P3OT** regardless large difference in their solubilities

The obtained results suggest that molecular structures of some fullerene derivatives have stronger influence on the morphologies of their blends with P3OT and P3DT (P3ATs with long side chains) than solubility of these compounds in the solvent used for thin film deposition. Fullerene derivatives with long linear solubilizing groups (propyl, butyl) give the best results in combination with polymers possessing long alkyl side chains (P3OT, P3Dt, P3DDT). This observation points on the existence of some favorable supramolecular interactions between the side chains attached to the donor and acceptor molecules in the photoactive blends. Branching of the side chains attached to the fullerene results in larger phase separation and lower photovoltaic performance. This effect becomes more and more pronounced with increase in the length of the side chain attached to the polymer backbone.

## References

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## Future collaboration with host institution

The obtained results are considered as promising and intriguing. However, further elaboration of the fullerene derivative/P3AT composite systems is required. Particularly, additional experiments are required to clarify solubility trends for polymers P3BT and P3DDT. We did not show results for these two polymers since they are not reproducible well enough. At the same time, the systematic study will benefit from investigation of two additional polymers: poly(3-pentylthiophene) **P3PT** and poly(3-heptylthiophene) **P3HepT**. These polymers have side chain length close to the best performing polymer P3HT. Therefore, high photovoltaic efficiencies might be expected for composites of these polymers with fullerene derivatives. Application of few additional fullerene derivatives will also be very helpful.

In conclusion, further collaboration will be focused mainly on continuation of the initiated studies of the fullerene derivative/poly(3-alkylthiophene) composite systems.

## Projected publications

When this study will be completed, we plan to publish results in one large full paper, most probably submitted to *Advanced Functional Materials*. Preliminary results might be also presented at the conferences TPE 2010 in Rudolstadt and EMRS Spring Meeting 2010 in Strasbourg.

## **Acknowledgements**

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