

Scientific Report

on the

Exchange Grant

“Adjustment of material solubility as a way for optimization of bulk morphology and photovoltaic performance of composites comprising conjugated polymers with increased oxidation potentials and various fullerene derivatives”

within the ORGANISOLAR-Program
of the European Science Foundation

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Exchange Period: 5th October 2009 – 15th November 2009

Reference Number: 2555

1. Purpose of the visit

One of the promising ways to improve organic photovoltaics is to design novel conjugated polymers with reasonably high oxidation and ionization potentials. These materials have lowered HOMO energy levels that allow one to obtain higher open circuit voltages in the photovoltaic devices. Very promising results were obtained recently for a fluorene-based copolymer **PF10TBT** with di(2-thienyl)benzo[c][1,2,5]thiadiazole. Organic solar cells based on a combination of this material with [60]PCBM yielded open circuit voltage of 1.00-1.05 V and overall power conversion efficiencies of 4.0-4.5% [D. Veldman et. al., J. AM. CHEM. SOC. **2008**, *130*, 7721–7735]. It is notable that optimized solar cells comprise only 20% of **PF10TBT** as donor polymer and 80% of [60]PCBM. It is reasonable to replace [60]PCBM by [70]PCBM which harvests light much more efficiently in the visible range. For instance, 30% increase in the photocurrent was achieved by use of [70]PCBM instead of [60]PCBM in conventional MDMO-PPV based solar cells []. Therefore, one can expect that combination of **PF10TBT**/[70]PCBM might give solar cells with power conversion efficiencies exceeding 5.5%. However, our preliminary experiments showed that [70]PCBM gives much worse results in the blends with **PF10TBT** than conventional [60]PCBM.

We believe that the reason for poor photovoltaic performance of the **PF10TBT**/[70]PCBM blends is their non-optimized bulk morphology. 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 [*Adv. Funct. Mater.* **2009**, *19*, 779]. It is very likely that similar solubility-related effects play a significant role in the case of **PF10TBT**-based systems.

In the frame of the present project we plan to investigate thoroughly **PF10TBT (P3)** and two related polymers (**P1-P2**) with shorter side chains provided by Dr. Sergey Ponomarenko from ISPM RAS. At the same time, a series of novel copolymers **P4-P6** provided by Dr. D. Egbe from LIOS will be also investigated (Figure 1). These copolymers have wider band gaps than **PF10TBT** polymer but possess very similar HOMO energy levels. Therefore they also should give open circuit voltages of ~1.0 V.

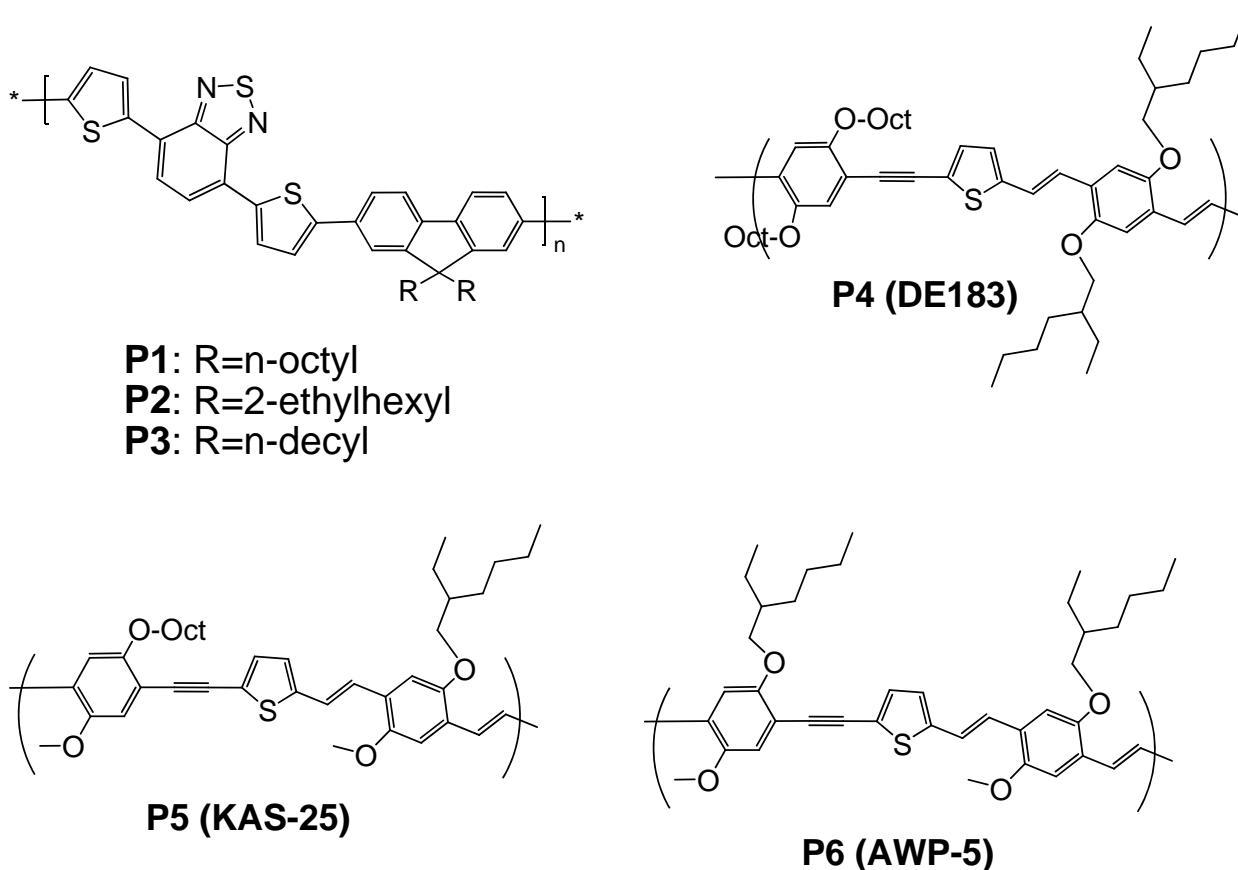


Figure 1 Molecular structures of the investigated polymers

2. Description of the work carried out during the visit

Initially all studied polymers were combined with conventional fullerene-based material [60]PCBM. Obtained PCBM/polymer composites with variable component ratios were investigated as active layer materials in organic solar cells (layout of the cell is shown in Figure 2). This preliminary test allowed us to get some impression about photovoltaic performance of all materials. On the next step the most promising polymer was combined with various fullerene derivatives possessing different solubilities in organic solvents. Variation of the fullerene-based material allowed us to manipulate active layer morphology.

A plan of the studies performed in the frame of the visit to LIOS can be summarized as follows.

- Comparative study of all polymers **P1-P6** in solar cells together with [60]PCBM as electron acceptor material.

- Investigation of the best performing polymers in combination with series of fullerene derivatives possessing different solubilities.
- Evaluation of the active layer morphology for all investigated composites using optical and AFM microscopy.
- Analysis of the obtained data to reveal correlations between the material structure and solubility on the one side and blend morphology and its photovoltaic performance on the other.

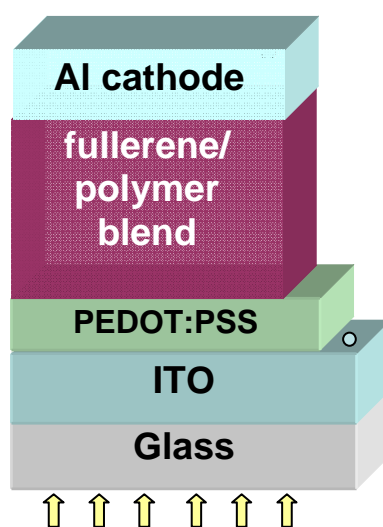


Figure 2 Layout of the investigated bulk heterojunction organic solar cell

3. Description of the main results obtained

3.1 Comparative study of all low band-gap polymers in solar cells together with [60]PCBM as electron acceptor material

Output parameters of organic solar cells comprising polymers **P1-P6** are summarized in Table 1. It is seen from these data that polymer **P1** showed the highest power conversion efficiency of 3.5% in combination with [60]PCBM. All other polymers showed much lower performances that might be related to the following reasons.

1. Large optical band gaps lower significantly achievable photocurrent densities in the case of polymers **P4-P6**.
2. Unfavorable molecular structure, for instance, large and branched solubilizing side chains (like 2-ethylhexyl in the polymer **P2**), might lead to lowered photovoltaic performances.
3. Insufficient material purity might be another issues severely limiting performance of the investigated polymer materials. Catalyst impurities or traces of some reactive organic reagents might work as efficient charge traps thus

inhibiting photocurrent generation. Device fill factors might also fall down in this case because of the accumulation of the trapped charges in the active layer. This seems to be the case of the polymer **P3** which should perform much better in solar cells according to the literature data [1].

Table 1. Output parameters of organic solar cells comprising polymers **P1-P6**

System	Ratio	I _{SC}	V _{OC}	FF, %	PCE, %
P1	1:4	9.7	900	40	3.5
P2	1:4	7.65	950	35	2.5
P3	1:4	4.28	950	41	1.7
P4 (DE-183)	1:1	3.23	900	37	1.1
	1:2	2.82	900	47	1.2
P5 (KAS-25)	1:1	2.36	900	31	0.7
	1:2	5.75	880	44	2.2
	1:3	4.8	780	37	1.4
	1:4	4.0	820	38	1.3
P6 (AWP-5)	1:2	3.9	850	38	1.3
	1:3	5.5	850	42	2.0
	1:4	4.6	850	37	1.4

3.2 Investigation of the polymer **P1** in combination with series of fullerene derivatives possessing different solubilities

We focused our further studies on the polymer **P1** as the most efficient and promising material. In this part of work we applied a family of 12 fullerene derivatives possessing different solubilities as electron acceptor counterparts for blending with the polymers. Molecular structures of these compounds are not shown in this report (publication is planned). We expected to observe some solubility dependence with a single maximum similar to the one previously revealed for P3HT-based composites [2].

The experimental results obtained for the polymer **P1** are shown in Figure 3. It is clearly seen from the plots that both short circuit current densities (I_{SC}) and power conversion efficiencies (η) steadily decrease when the solubility of the fullerene component is increased. Both curves have their maxima at solubility level of 20-30 mg/ml. Unfortunately we cannot follow the solubility trends below limit of 20 mg/ml because lower concentrations of the fullerene component did not allow the film preparation (note that the polymer concentration is ~5 mg/ml only).

The appearance of the maxima on the plots allows us to conclude that that polymer **P1** behaves similarly to the conventional polymer P3HT investigated previously [2]. The solubility of the fullerene component should be between 35 and 70 mg/ml to achieve optimal device

performance with P3HT. However, optimal solubility of the fullerene counterpart lies between 19 and 50 mg/ml for polymer **P1**. This difference might be a consequence of the lower solubility of the polymer **P1** in chlorobenzene which was estimated to be in the range of 20-30 mg/ml. For comparison, the solubility of P3HT in chlorobenzene estimated in [2] was 50-70 mg/ml. Thus, we revealed that maximal photocurrents and power conversion efficiencies are reached when the polymer **P1** is combined with the low soluble fullerene derivatives. This is the most promising direction for further optimization of the photovoltaic devices based on polymer **P1**.

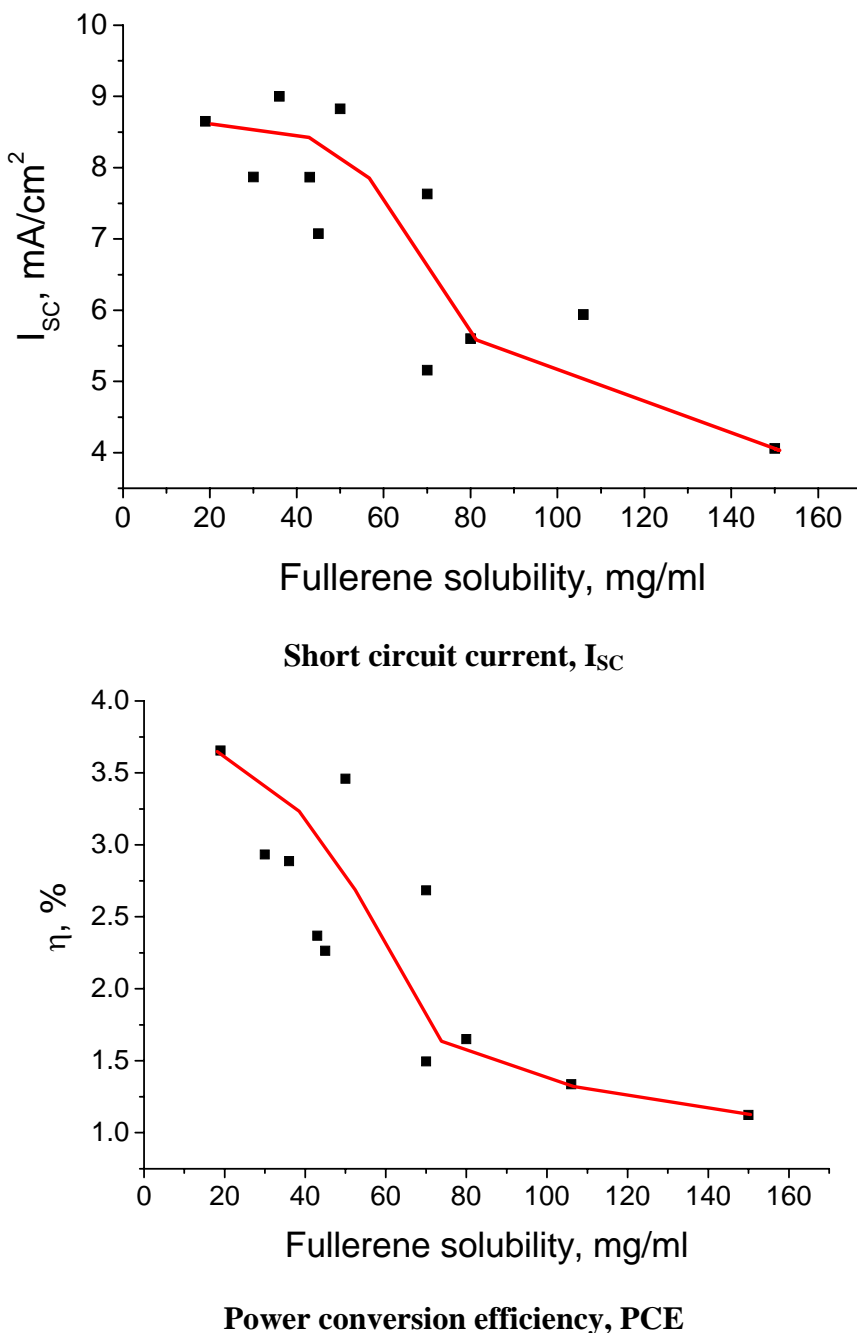
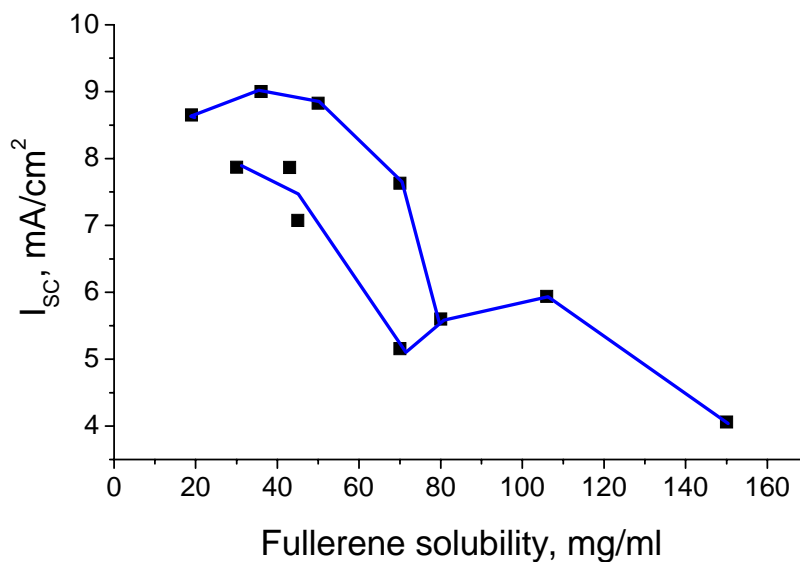
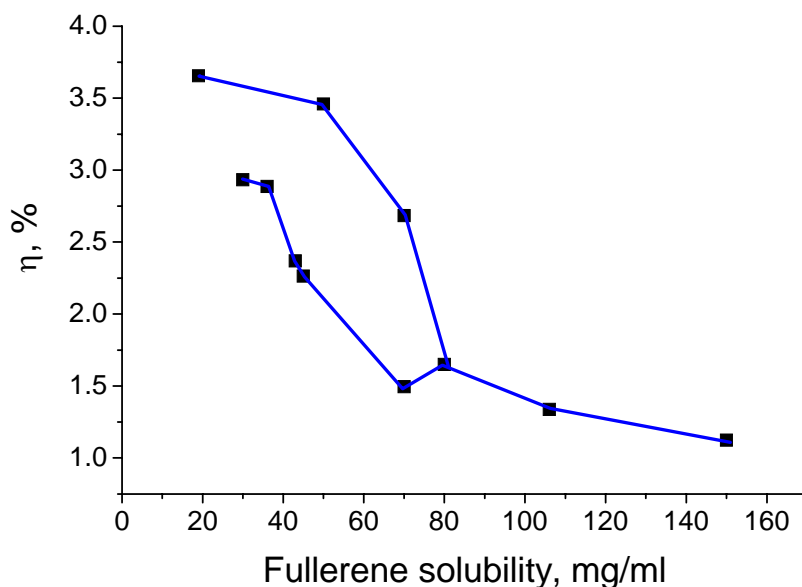


Figure 3 Output parameters of solar cells comprising polymer **P1** and various fullerene derivatives as a function of the solubility of the fullerene component. Red lines are guides for the eye illustrating maxima on the plots at solubilities 20-0 mg/ml.

Deeper analysis of the photovoltaic parameters obtained for the blends of polymer **P1** with various fullerene derivatives suggest some double-branch solubility behavior for these systems which is illustrated in Figure 4. We plotted here the same data points as in Figure 3 and connected them with blue lines to mark proposed upper and lower branches of the curves appeared in the solubility range of 20-80 mg/ml. We note here that all presented data points were quite reproducible that minimizes the possibility of an experimental error.



Short circuit current, I_{sc}



Power conversion efficiency, PCE

Figure 4 Output parameters of solar cells comprising polymer **P1** and various fullerene derivatives as a function of the solubility of the fullerene component. Blue lines are guides for the eye indicating proposed double-branch solubility behavior.

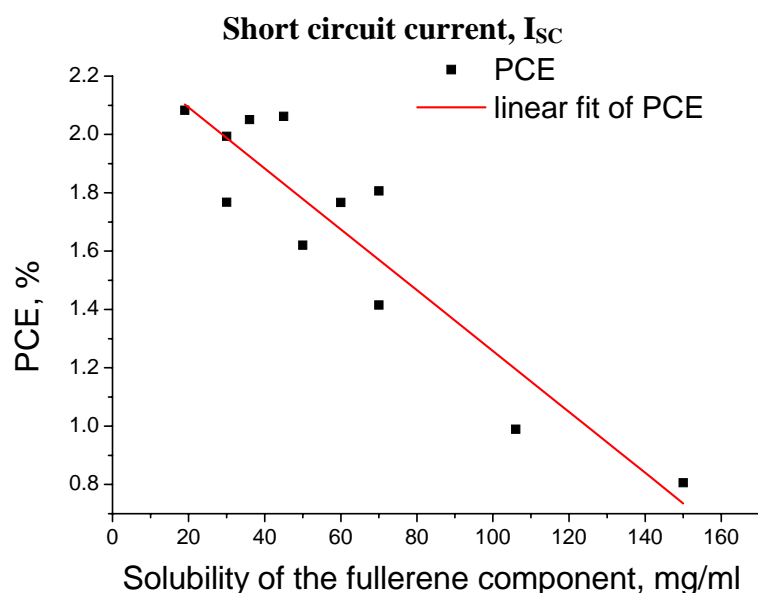
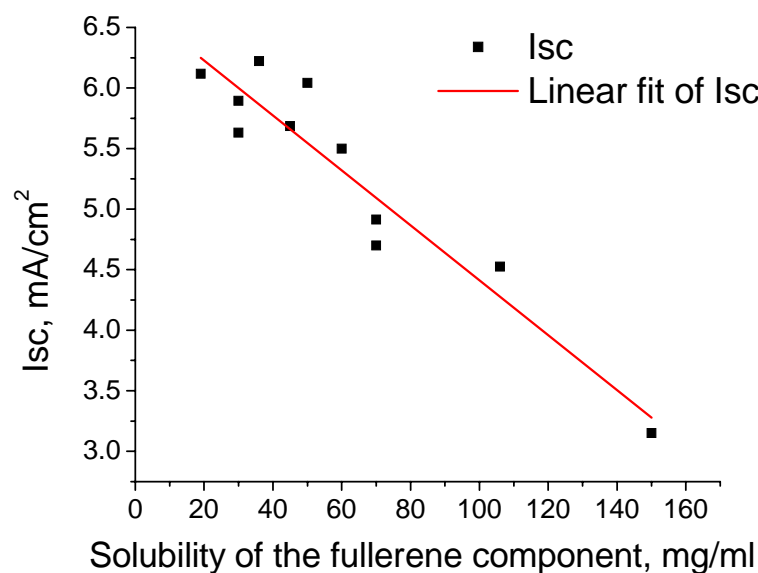
Similar double-branch solubility behavior was observed for some other polymers investigated by my colleagues Dr. Pavel A. Troshin and Mrs. Diana K. Susarova (see their reports). The appearance of the double-branch solubility behavior suggest that some fullerene derivatives are better compatible with the polymer **P1** than others. This compatibility seems to be independent on the solubility of the fullerene-based material and, most probably, is dictated by some peculiarities of their molecular structures.

3.3 Investigation of the polymer P6 in combination with series of fullerene derivatives possessing different solubilities

We performed the polymer **P6** similar studies as described above for polymer **P1**. The selection of this material was motivated by its availability in large quantities and its reasonable photovoltaic performance. Other polymers (**P2-P5**) were available in very limited quantities that did not allow their systematic investigation.

The results obtained for the polymer **P6** are depicted in Figure 5. It is seen from these plots that both I_{SC} and power conversion efficiencies decrease almost linearly upon increase in the solubility of the fullerene component. These linear solubility trends we observed for the first time. Therefore **P6** behaves differently in comparison with P3HT on one side, where single maximum solubility dependence was observed [2] and, on the other side, in comparison with the polymers that revealed double branch behavior (such as **P1** and few other polymers investigated in our group). Unusual monotonously linear solubility behavior of the systems composed of **P6** and different fullerene derivatives is most probably related to specific molecular structure and physical properties of this polymer. This issue requires further investigations that will be carried out in future.

We point out that polymer **P6** gives the best photovoltaic performances in combination with the low soluble fullerene derivatives that makes it similar to the polymer **P1** described above. Therefore, further optimization of the solar cells based on polymer **P6** should be based on the fullerene derivatives with solubility of 15-30 mg/ml.



Power conversion efficiency, PCE

Figure 5 Output parameters of solar cells comprising polymer **P6** and various fullerene derivatives as a function of the solubility of the fullerene component. Red lines are guides for the eye indicating linear solubility behavior.

3.4 Evaluation of the active layer morphology for all investigated composites using optical and AFM microscopy

In order to investigate the effect of the solubility of the fullerene derivatives on the morphology of their blends with polymers **P1** and **P6** we performed AFM studies for all prepared fullerene/polymer composites. However, AFM studies did not reveal substantial differences in the surface topology of the investigated blends (Figure 6).

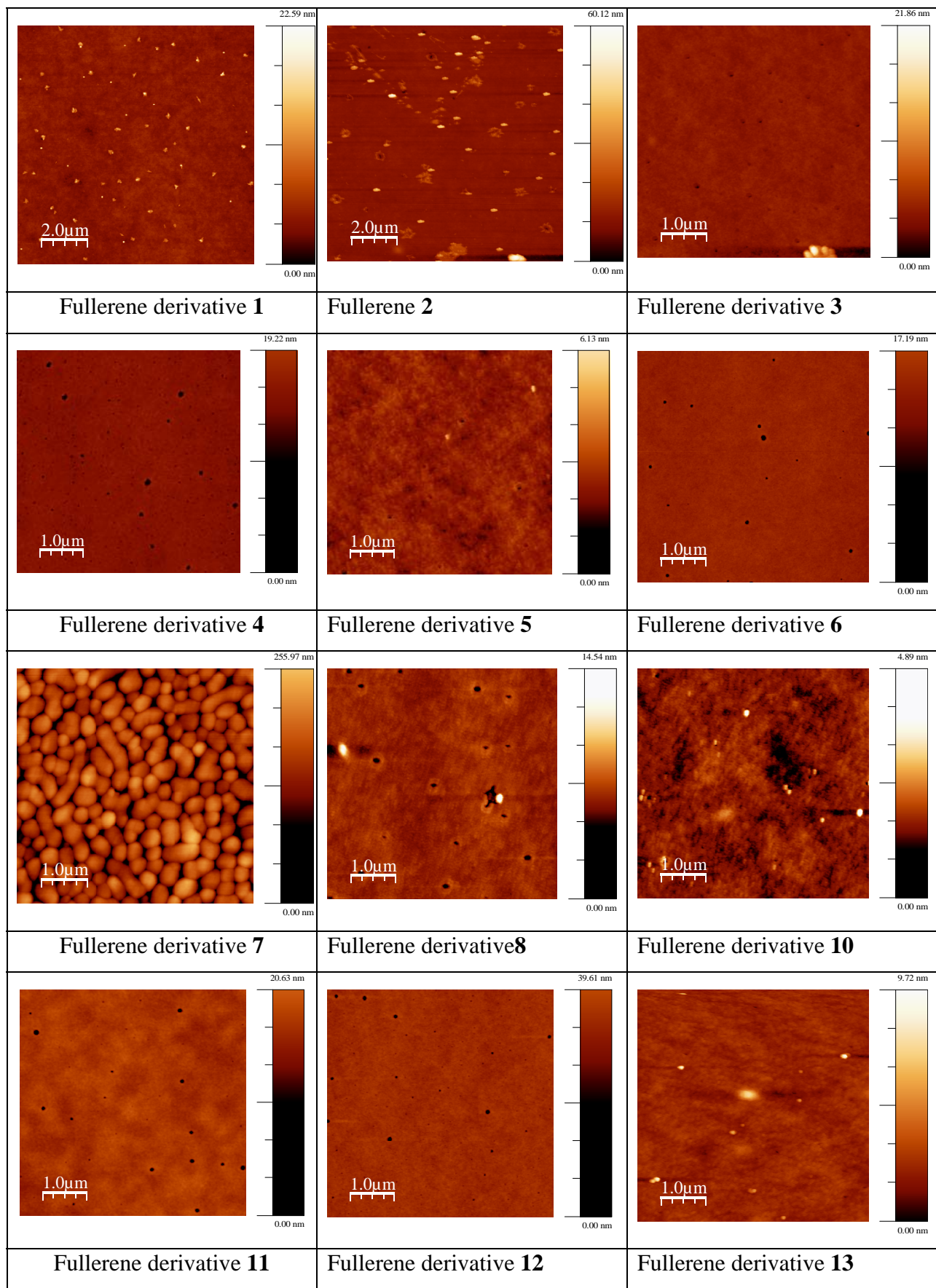


Figure 6 AFM topology images of the blends composed of the polymer **P1** and different fullerene derivatives

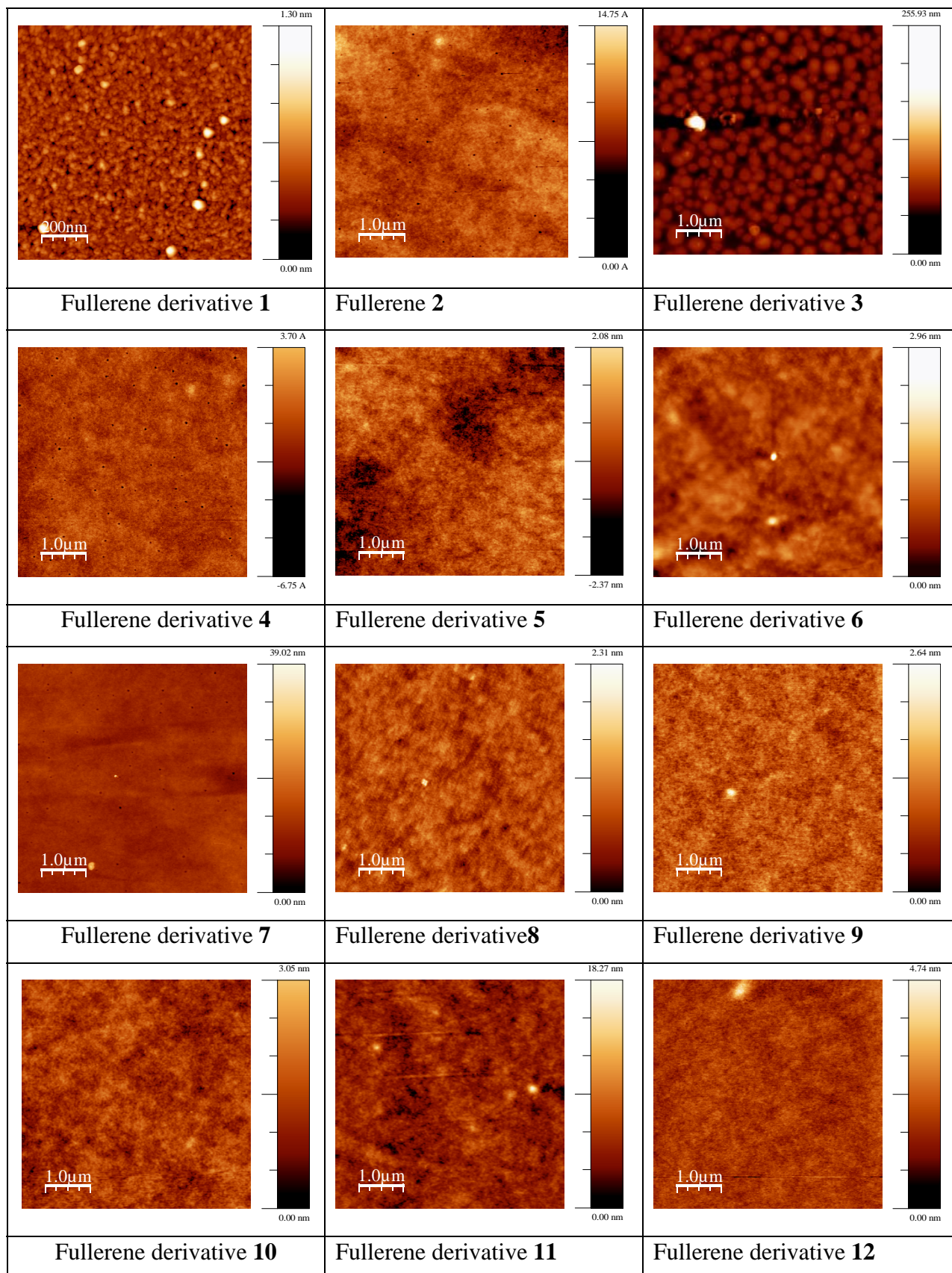


Figure 7 AFM topology images of the blends composed of the polymer **P6** and different fullerene derivatives

In the case of polymer **P1**, only one system (fullerene derivative No. 7) exhibited significant surface granularity suggesting large scale phase separation between the components in the blend. This system, as could be expected, performed poorly in photovoltaic devices. Some other systems (fullerenes 1 and 2) showed numerous irregularities on the film surface. These hills are suspected to be small clusters of fullerene derivatives segregated from the blend. It is notable that such systems showed the best performances in organic solar cells. On the contrary, blends exhibiting multiple holes or craters on the films surface (fullerenes 4, 6, 8 and etc.) demonstrated lower photovoltaic performances.

In the case of polymer **P6**, one fullerene derivative (No.3 in Figure 7) again induced surface granularities suggesting large scale phase separation between the components in the blend. All other measured AFM images were more or less featureless. However, in spite of the very similar flat surface topologies, these blends might have quite different bulk morphologies. However, investigation of such “masked” blend morphology requires application of some other microscopy techniques (perhaps, TEM) penetrating deeper into (or even through) organic films.

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Future collaboration with the host institution

We obtained interesting results related to the solubility behavior of the blends composed of the polymers **P1** or **P6** and various fullerene derivatives. It was clarified what kind of fullerene based acceptor materials should be combined with **P1** and **P6** to achieve the best photovoltaic performances. Further research in that direction might bring new important fundamental results as well as highly efficient material combinations for organic solar cells.

Our further collaboration with LIOS will be focused on the following issues.

1. Verification of the double-branch solubility behavior observed for polymer **P1** is an important task that should be solved in the nearest future. On the one hand, all recently obtained results should be reproduced additionally few more times. Statistical treatment of the data will allow us to improve accuracy of the results. On the other hand, larger number of fullerene derivatives should be involved in the study in order to increase number of the data points on the solubility plots.
2. Investigation of the solubility trends for other polymers with relatively high oxidation potential. These polymers are currently being synthesized at IPCP RAS and LIOS.
3. When the overall data set will be sufficiently large, we will focus our efforts on elaboration of some theoretical model that should predict with reasonable accuracy solubility trends for any novel polymer.

Projected publications

Results of this work will be presented as a part of a larger publication in the nearest future. Preliminary results will be also included in the presentations at the conferences TPE 2010 in Rudolstadt and EMRS Spring Meeting 2010 in Strasbourg.

Acknowledgements

I thank my colleague Diana Susarova who helped me a lot with my studies at LIOS. I also thank Prof. Sariciftci as a Director of the Host Institution and all other members of LIOS for providing unique facilities for conduction of this work, kind support and cooperation.

Financial support from ESF is gratefully acknowledged.