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Review of the Doctoral Thesis "Przewodzące nanoszczotki polimerowe o strukturze donorowo-akceptorowej" elaborated by mgr Anna Grobelny at the Faculty of Chemistry of the Jagiellonian University in Kraków under the supervision of prof. dr hab. Szczepan Zapotoczny

The thesis of Anna Grobelny presents a fascinating and relevant topic related to organic donor-acceptor semiconductors for applications in solar cells. Solar cells play an important role for the transformation of the energy sector from fossil fuels to ecological and sustainable sources. So far, the commercial solar cells are based on inorganic semiconductors, mainly silicon, that show high efficiencies and long lifetimes. Alternative concepts are based on organic semiconductors that bear potential for low-cost, low-weight and mechanically flexible devices opening the door towards new technologies. The organic semiconductors are based on conjugated molecules, either small molecules or polymers. Attachment of side chains allows to tune their solubility in organic solvents and therefore a film deposition by wet techniques. Conjugated polymers based on donor and acceptor units in the backbone show the highest potential for solar cells due to a narrow energy bandgap and thus high light absorption resulting in good device efficiencies in comparison to other organic semiconductors. However, organic solar cells still suffer from moderate efficiencies in comparison to inorganic ones and poor stabilities limiting their practical application.

To solve the problem of poor film stability of organic semiconductor films, Anna Grobelny developed in her doctoral work polymer brushes based on the donor-acceptor units. Polymer brushes are covalently bonded to the substrate surface, typically an electrode in the solar cell, and ensure in this way an improved stability of the film. A further advantage of the perpendicularly oriented polymer backbones is a more effective charge carrier transport in the device. Additionally, a solubility of the conjugated polymer is not necessary for the film formation.

The thesis of Anna Grobelny was prepared at the Faculty of Chemistry of the Jagiellonian University in Kraków under the supervision of prof. dr hab. Szczepan Zapotoczny. The thesis contains 182 pages, is well structured and well written in Polish language. The figures, tables and equations have been prepared with care. Special attention of the reader is drawn to the uniformity of all schematic illustrations that are prepared in the same style and coloristics.

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Tables are also kept in the same color so that the whole thesis forms a homogenous unity. There are no formal mistakes which could be criticized.

After acknowledgments, the thesis begins with the table of contents followed by the abstract written in both Polish and English. After the list of figures, schemes, tables and abbreviations, the motivation part provides a general introduction to the topic, the methodology, and aim of the thesis. The main core of the thesis is divided in two key chapters. Chapter 8 gives a literature overview, and Chapter 9 discusses the experimental results. The thesis is closed with the summery, reference list and academic achievements such as the publication list and conference contributions of Anna Grobelny.

The first part of the literature overview in Chapter 8 is dedicated to the general introduction to the field of (semi-)conducting polymers and their application in electronics. Especially Table 1 shows a good summery about the synthesis concepts for conjugated polymers. This type of summery table is later also presented in other subchapters providing a good overview to the reader and maintaining an identical style for the literature part. Thereafter, donor-acceptor polymers are introduced as one important aspect of the thesis. The formation of the narrow bandgap and its importance for solar cells are clearly explained. Different configurations and building blocks of donor-acceptor polymers are discussed followed by reviewing the key reactions for the synthesis of these polymers. The final part of the literature overview is focused on polymer brushes and starts with the discussion on film deposition on surfaces and the advantages of polymer brushes. The presentation of the synthesis of different types of polymer brushes is very comprehensive providing an excellent overview. The last topic of this subchapter is dedicated to conducting polymer brushes and emphasizes that donor-acceptor ones are rarely reported so far.

The first part of the experimental Chapter 9 describes the applied materials, techniques, synthesis of the monomers including all their analytical characterization and grafting procedures. The discussion of the experimental results starts with the DFT calculations. This is a rational approach for selection of the most optimum molecular structure regarding the bandgap. The choice of different donor and acceptor building blocks and substituents is clearly explained. It was found that compound DA11 shows the smallest bandgap of 2.03 eV. In the next step, the synthesis of the monomers is described including unsuccessful routes and taking into account information from literature.

The synthesis of the polymer brushes was performed by different methods such as Sonogashiry, Stille, Click, PIMP, RAFT and ATRP. In the case of Sonogashiry, the layer growth reaches after new layers a constant thickness what is related to various defect formations as illustrated

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in Figure 24. Another interesting aspect, observed also for other polymer brushes that are described later in the thesis, is the UV-Vis absorption with increasing layer number. This behavior is related to the effect of the molar absorption coefficient of the molecule. The density of the brushes was tuned by changing the ratio of the APTES and ClPTES units on the surface. As another interesting observation, the film thickness increases with lower grafting density what is explained by conformation changes and an improved packing of the molecules. Similar results are observed for the brushes obtained by the Click reaction, while layers obtained by Stille reveal a small dependence on the grafting density. The conductivity measurements of the film obtained by Sonogashiry were performed by peakforce AFM revealing a value of $8 \cdot 10^{-6}$ $S \cdot cm^{-1}$.

While the above applied reaction procedures were successfully applied, SI-PIMP did not allow to create films in a repeatable manner. For this reason, SI-RAFT procedure was followed and optimized. Thereby, the film thickness closely depended on the reaction time and grafting density. A dependence of the film thickness on the reaction time were also observed for poly(8-alt-9) layers synthesized by PTH-RAFT. The poly(8-alt-9) brushes were turned in the next step into ladder-type structures. An increase in film thickness and change in film morphology were noticed, whereby the films did not show any conductivity what was related to the large energy bandgap. The RAFT procedure was also used to obtain layers based on poly(St-alt-13) and a dependence of the film thickness on the reaction time was also monitored. Changing the polymer brushes into ladder-type resulted in a drop of the film thickness what was attributed to the steric hindrance of the aryl groups. To improve the conductivity of the film, the polymer brushes were doped by iodine leading to a value of $4 \cdot 10^{-6}$ $S \cdot cm^{-1}$.

The development of these donor-acceptor polymer brushes is remarkable and the analysis and discussion of the results have been performed with much care, however, there are few points that need further clarification.

- A general question is related to the linkage of the polymers to the surface. In solar cells, the grafting would take place to an electrode. However, the linkage to the polymers is never conjugated. Is this a potential barrier for the charge injection from the electrode to the polymer brushes?
- The ellipsometry data in Figure 23 shows a quite constant film thickness with higher number of layers. However, the AFM images in Figure 28 show a stronger thickness increase from 5. to 10. layers. Are both methods in contradiction to each other?
- Is any analytical indication possible to confirm structural defects that are illustrated in Figures 24 and 35?

- What is the reason higher contact angle of the donor layer observed in Figure 27? Similar effects are also observed for the other polymer brushes in the thesis
- Some maximum conductivity peaks appear in the scan in Figure 33C. What is their reason?
- Is the conductivity of $8 \cdot 10^{-6}$ $S \cdot cm^{-1}$ high and can this value be compared to literature values?
- The contact angle in Figure 41 shows one outliner for 6 layers deposited on quartz substrate. Is this an experimental error or indeed a higher contact angle just for 6 layers?
- Figure 49A shows an AFM topology of poly(8-alt-9) obtained by RAFT. What is the thickness of this film? The topology significantly differs from the images in 49B and 49C. Is there any reason for a different topology?
- The AFM images in Figure 54 show a topology of many drops/islands. Can this topology originate from dewetting? The height of these drops reaches maximum height up to 150 nm. However, this is not in accordance with the film thickness determined by ellipsometry. Does the ellipsometry provide average results, while the AFM images show a more detailed picture?
- The polymer backbone of both poly(St-alt-13) and poly(8-alt-9) is not conjugated. Is this the reason for the lack of conductivity of the corresponding ladder-type polymers?

In summary, Ms. Grobelny has confirmed her competency on the field of the synthesis and characterization of conjugated polymer brushes. Her research methodology has been prepared in a senseful and clear manner and the research as well as analysis of the results has been performed with high competence and care leading to comprehensive interpretations and conclusions.

The publication record of Ms. Grobelny in the frame of her thesis is very good. She is (co-)author of five papers published in high-ranking international journals (one manuscript is currently in review), with three of them as first author. The active participation in many scientific conferences and research projects as well as impressive number of awards confirm her intensive involvement in her research.

Therefore, in my opinion the reviewed thesis fulfills the statutory criteria set for the doctoral dissertations in Article 13, Paragraph 1 of the Act of 14 March 2003 and I ask for admission of Anna Grobelny to the public defense of the dissertation.

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