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Oponentní posudek

na diplomovou práci Bc. Milana Klikara s názvem

"Barbiturová kyselina jako akceptorní část v push-pull chromoforech"

π-Conjugated organic molecules are an important class of materials for organic optoelectronic devices, such as light-emitting diodes (OLEDs), field effect transistors (FETs), solar cells, and nonlinear optics (NLO). In particular, push-pull chromophores consisting of potent electron donor and acceptor moieties connected through various π-conjugated linkers have attracted considerable attention. Due to their strongly bathochromically shifted UV/vis absorption bands they are of interest either as functional dyes for NLO or as solar absorbers in bulk heterojunction organic solar cells.

As an integral part of the continuing research efforts of the Bureš group on functional organic chromophores, the presented Diploma thesis of Bc. Klikar aimed at the synthesis and investigation of a series of push-pull chrompohores incorporating *N,N'*-dibutylbarbituric acid electron acceptors and *N,N*-dimethylanilino donors. The influence of the π-conjugated spacer interconnecting the donor and acceptor moieties on the optoelectronic properties of the resulting chromophores was studied by both experimental and theoretical methods.

In the Theoretical Part (Chapter 1; 31 pages) of the thesis, Bc. Klikar introduces barbituric acid and its derivatives and discusses various synthetic approaches towards these versatile compounds. Furthermore, a brief theoretical background of intramolecular charge-transfer (ICT) interactions and NLO phenomena is provided. The main focus of this chapter is, however, an extensive overview of known push-pull chromophores involving barbituric and thiobarbituric acid derivatives, their properties and application. While there is no doubt that this part is based on a careful literature search, it is somewhat lengthy and imbalanced with respect to the rest of the thesis. Overall, Chapter 1 with its 31 pages constitutes almost 40% of the total thesis volume (Appendix excluded) and hence stands in a sharp contrast with Chapter 3 discussing the obtained results within only 15 pages. From my standpoint, the derivatives of thiobarbituric acid, that were not the subject of the thesis, might have been omitted to increase the readability of this part. In Chapter 1, as well as in the remaining part of the thesis, typos appear only sporadically, nevertheless, several points regarding this part should be mentioned:

i. Page 16: "Hantzsche-Widmana" instead of "Hantze-Widmana".

ii. Page 18: Why the part 1.1.4. does not involve any citation?

iii. Page 26, Scheme 8: The abbreviation "l.t." which obviously stands for "laboratorní teplota" does not appear in the list of abbreviations.

iv. Page 31, Table II: Instead of $\beta_0 \cdot 10^{30}$ must be $\beta_0 \cdot 10^{-30}$.

v. A single page at the end of Chapter 1 summing up the reasons (motivation) that stimulated the described research efforts would have been highly beneficial for the thesis.

The Experimental Part (Chapter 2; 28 pages) is concisely written, the synthesized compounds are rigorously characterized, and the relevant published work is properly cited. Besides of the rather unlucky representation of the *E*/*Z* isomerism in compound **87** (Page 53) and missing elemental analyses, there is hardly any reason for criticism. It is not only the impressive amount of synthetic work performed by Bc. KLIKAR during the limited time of his Diploma thesis that must be pointed out here but also his eye for detail that becomes obvious after reading this chapter.

As detailed in Chapter 3 (Results and Discussion; 15 pages), a series of 12 push-pull chromophores differing in the type and length of the π-conjugated spacer between the acceptor (*N*,*N*'-dibutylbarbituric acid) and donor (*N*,*N*-dimethylanilino) moieties have been synthesized. The key step in their synthesis was a Knoevenagel condensation between the corresponding aldehyde, prepared typically by Pd-catalyzed cross-coupling reactions from synthetically well-accessible precursors, and *N*,*N*'-dibutylbarbituric acid (also synthesized by Bc. KLIKAR by following literature procedures). Whereas the synthesis and purification of the chromophores **CH1** and **CH5-12** was rather unproblematic, compounds **CH2-4** decomposed during attempted column chromatography. Due to these difficulties, Bc. KLIKAR searched for alternative routes towards the desired chromophores. For this purpose, *N*,*N*'-dibutylbarbituric acid was condensed with the iodinated precursor aldehyde and the *N*,*N*-dimethylanilino donor was attached in the subsequent Pd-catalyzed cross-coupling reactions. However, this approach did not bring any improvement as it either delivered lower yields or failed completely in several cases. In spite of these rather disappointing findings, the enthusiasm and initiative of Bc. Killar to systematically seek a solution for the encountered problems must be recognized; in fact, such ability is rather rarely seen at this educational level.

As already mentioned above, all target compounds **CH1-12** were fully characterized by standard physicochemical techniques but elemental analysis. This is rather surprising, as the purity of functional organic compounds is crucial with respect to their photophysical characteristics (*e.g.* NLO) and, of course, to their final device application. As to that, it is incorrect to consider high-resolution mass spectrometry or X-ray crystallography as unambiguous purity proofs. Also NMR spectroscopy might be misleading due to its limited sensitivity and possible presence of NMR inactive impurities.

In addition, a detailed discussion of the obtained electrochemical, UV/vis, and X-ray crystallographic data (**CH1** and **CH5**) is provided. Supported by computational studies, all data point towards pronounced intramolecular charge-transfer character and relatively high first

hyperpolarizabilities β of the synthesized chromophores **CH1-12**. While taking into account all experimental and theoretical data, chromophores **CH7** and **CH11** were identified as particularly promising candidates for further photophysical studies followed by application in organic optoelectronic devices. Again, this part of the thesis is concisely written and reads well, nevertheless, several remarks and questions need to be raised:

i. It is obvious that some of the studied chromophores can exist as *E*/*Z* isomers, however, nothing has been said about their configurational stability upon irradiation. This certainly needs to be clarified before publication.

ii. Page 76 and 77, Scheme 36 and 37: Both schemes are rather crowded and the use of the "wavy bond" to express the different π-spacers does not make the situation any better. To draw fully the particular structures would have significantly contributed to clarity, at least in my eyes. It would have been also easier for the reader to indicate particular reagents (and conditions) in the schemes instead of referring to general methods **A-D**, which requires going back and forth between Chapter 2 and 3.

iii. To prove the charge-transfer character of the longest-wavelength absorption bands in the UV/vis spectra, so-called protonation/deprotonation experiments are commonly used. Has Bc. KLIKAR performed such experiments for some of his chromophores and is he able to explain the principle of the observed phenomena?

iv. Page 89, Figure 29: The figure is too small, the HOMO/LUMO colors are not luckily chosen, and it is not clear at first sight which orbital is which. Better labeling would have readily solved this problem.

In summary, the present Diploma thesis of Bc. KLIKAR meets all mandatory objectives set and clearly demonstrates his ability to plan his work upon exhaustive literature searches, his excellent experimental skills, and, most importantly, his ability to analyze and interpret the obtained data and observations. After reading carefully the thesis, I have absolutely no doubt that Bc. KLIKAR possesses the capacity to scholarly present his work and results. This ability is, however, somewhat ruined by the poor print quality of the thesis. I assume that the results obtained within this Diploma research project will soon lead to a publication in some of the peer-reviewed journals. Therefore, I personally find rather pity that the thesis has not been written in English.

Z výše uvedených důvodů doporučuji předloženou diplomovou práci Bc. MILANA KLIKARA k obhajobě a hodnotím ji známkou

– VÝBORNĚ –

Dr. Milan Kivala