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Review report on the PhD dissertation of Ms. Martyna DURKO-MACIAG.

Ms. Martyna DURKO-MACIAG has performed her thesis research work under an interdisciplinary cross-institutional post-graduate studies KNOW between Wroclaw University of Science and Technology in Poland under the supervision of Prof. Jaroslaw MYSLIWIEC and French National Centre for Scientific Research and University of Strasbourg in France under the supervision of Dr. Julien MASSUE. The research work thesis is entitled " **Chare Transfer Compounds as Sources of light**".

The main goal of the PhD thesis is primarily to develop light amplifying systems and possibly to determine (through fundamental characterizations based on absorption and emission spectroscopies) the pumping conditions for the stimulated emission to occur. Secondly, since the majority of the organic lasers are designed in the solid state, Ms. Martyna DURKO-MACIAG has inspected the influence of the both aggregation and crystallization on the emissive properties of the compounds prepared. For that, Ms. Martyna DURKO-MACIAG has designed and investigated noncommercially available materials that exhibit Excited-State Intramolecular Proton Transfer (ESIPT). The majority of the compounds used in the thesis are based on 2-(2'-hydroxyphenyl)benzoate scaffold. Modifications on the scaffold have been performed whether by changing the nature of the heteroatom or the variations of the π-conjugated substituents on the scaffold. Ms. Martyna DURKO-MACIAG, has then studied the influence of such modifications on the photophysical properties of the resulting compounds. She has also studied two Schiff bases that contains both an electron donor and an electron acceptor parts in which² an intramolecular charge transfer (ICT) is established. Finally, the possibility to obtain random or distributed feedback lasing was investigated in the thesis as well as the possibilities to use ESIPT type compounds for possible lasing applications have been estimated.

The thesis manuscript of Ms. Martyna DURKO-MACIAG is divided into two complementary parts. The first part is being dedicated to a theoretical introduction which starts with 1) the fundamental aspects of light-matter interaction, 2) a general introduction on organics chromophores and 3) light amplification. The second part is dedicated to the experimental investigations and its describing 1) materials and methods used, 2) the experimental results, 3) the different applications and ends with general conclusions as well as possible applications and perspectives. The entire manuscript contains 144 pages, is written in an excellent English and is very well illustrated. All these make an easy reading of the manuscript.

In the **theoretical introduction** part, entitled, "**Light-matter interaction: fundamental aspects**" the focus has been mainly defined on few fundamental processes related to matter-light interaction. The basic optical effects such as absorption, relaxation, scattering of light, aggregation effects, excited-state intramolecular proton transfer and finally light amplification phenomena such as spontaneous and stimulated emission, laser, amplified spontaneous emission, random lasers, distributed feedback and it ends with the organics chromophores that are mainly used in light amplification processes. These effects can serve for the understanding of more complex phenomena such light amplification.

In the **experimental investigations** part, the PhD student reported the chosen organic compounds used during the thesis work, the materials used as well as the experimental results. Three families of compounds have been described. The first family is based on 2-(2'-hydroxyphenyl)benzoxazoles (HBO) derivatives. Nine different compounds that differ by the nature and the number of the substituents on HBO scaffold have been reported. The second family is based on 2-(2'-hydroxyphenyl)benzimidazoles (HBI) and is composed of four different compounds. The third family is based on 2-(2'-hydroxyphenyl)benzothiazoles (HBT) derivatives and contains three different compounds. It worth to note that the PhD students has conducted the organic synthesis of three different molecules that are **HBI-4,6-TIPS, HBO-4,6-TIPS** and **HBT-4,6-TIPS**. All the other compounds have been provided by Dr. Julien MASSUE. The author has described the synthesis that she has performed for the three previously cited compounds. A description of the materials and methods used during the experimental investigations have then been reported. The experimental results chapter reports a presentation and discussion of the obtained experimental results on the ESIPT investigated compounds.

Ms. Martyna DURKO-MACIAG has therefore reported the photophysical properties of the ESIPT compounds, and has shown that all the investigated compounds exhibit ultraviolet light absorption and that are fluorescent in non-polar toluene solvent. The PhD student has made a careful comparison between the different emission of HBX compounds and has distinguished some major relationships between them. Thus, it has been shown that the spontaneous emission can be tuned by changing the nature of the heteroatom. Therefore, the fluorescence of the highest energies was obtained for the nitrogen analogs (HBI), then the oxygen analogs (HBO) and finally the sulfur ones (HBT). Also, the double substitution of these HBX compounds resulted in a bathochromic shift of the emission as compared with monosubstituted compounds. As expected, the introduction of electron donating or electron withdrawing groups resulted in additional electronic distribution. The analysis of both absorption and emission of all the compounds indicated a large Stokes shifts going from 7900 cm^{-1} for HBI-6-TIPS up to 11000 cm^{-1} for HBO-ext_NMe2. The absolute quantum yields calculated of the emission are varying from 4% up to 98%. In the case of the measurements in the solid state, the PhD student has shown the beneficial restriction of the intramolecular motion that resulted in higher quantum yields. An exception was observed with the quenching of the emission for the Schiff bases A-CN and A-F, however the ESIPT phenomenon was still present in the polymeric thin films that were doped with the different compounds.

Since the HBX studied compounds are fluorescent in solution, the investigation of Aggregation Induced Emission (AIE) indicated that six of the eighteen compounds exhibited AIEE properties, namely HBO-3-TIPS, HBO-4-TIPS, HBO-4,6-TMS, HBI-6-TIPS, HBI-4,6-TIPS and HBT-CF3-4,6-TMS. Note that the complete emission quenching was only observed for the two (A-CN and A-F) Schiff bases.

The PhD student has then investigated light amplification studies for all the eighteen compounds and has demonstrated that except for the (A-CN and A-F) derivatives, all the other sixteen 2-(2’-hydroxyphenyl)benzazoles mixed with polymeric thin films have shown light amplification process. The PhD student has demonstrated that the lasing action was achieved through a four level system based on the ESIPT photocycle. The optical feedback, in this case, is provided by multiple scattering. The molecular structure in the solid state (aggregates and/or crystallites) are responsible for the observed bathochromic shift as compared with the fluorescence. Note that a blue-green lasing was obtained for HBI derivatives, green for HBO derivatives and orange-red for HBT ones, covering therefore almost the whole visible spectrum. It has also been shown the nature of the polymeric matrix can be used to tune the stimulated emission because of the different interactions between the dyes and the polymer. It worth noting that amplified spontaneous emission (ASE) was obtained in concentrated solutions of the ESIPT compounds which proves the importance of these materials to be used as laser dyes.

Finally, the PhD students has used the obtained thin films as well as concentrated solutions of ESIPT compounds to achieve DFB lasers. Also, the possibility to use ESIPT compounds as DFB sensors has been evaluated. Of great importance and for the first time, the PhD student has shown that the anionic form of ESIPT can be used for stimulated emission. Mixing of two or three chromophores in sandwich-type structures led to the obtaining of white emission, with the possibility of switching between the emitted colors. Finally, the PhD student has show the possibility to use ESIPT compounds as photoinitiators in two-photon polymerization process that enables the fabrication of precise structures on a microscopic scale.

The present thesis work is showing very interesting results in the field of ESIPT materials, in particular in light amplification processes and in lasing applications in general. The PhD student has shown her competencies in both chemistry and physics and has clearly made a structure property relationship in order to explain the different photophysical and lasing properties that have been obtained.

I, referee (rapporteur) of this work highly recommend the Ph.D. defense of **Ms. Martyna DURKO-MACIAG** in order to obtain the Ph.D. diploma of Wroclaw University of Science and Technology.

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