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Report on the thesis manuscript presented by Anna Popczyk

« D-π-A type chromophores for light amplification and nonlinear optics applications»

The main goal of Anna Popczyk thesis work is the design of dipolar thiophene derivatives for different applications in optics or nonlinear optics. This project, which has been performed in co-tutelle between Wroclaw University of Science and Technology and Angers University, aims at addressing different issues, using an approach of an original molecular engineering, supported by systematic photophysical studies, rationalizing molecular structures and by the realization of devices for the demonstration of various physical effects and applications. This manuscript is structured in several parts (except experimental part), very clearly written, featuring numerous references. This document focuses on the description of the different concepts involved in the project, on the original molecular engineering approach, on the caracterisation of these new molecules and of the devices in which they are involved. This a work of a high quality, of which I will summarize below the main aspects.

The first chapter of this manuscript consists in an introduction to different fundamental concepts required in studies performed by Anna Popczyk on her molecules: ***spectroscopy*** (absorption, Jablonski diagram with all its mechanisms of relaxation, intermolecular energy transfer, intramolecular charge transfer, solvatochromism, dyes aggregation), ***nonlinear optics*** or NLO and its different phenomena (second and third harmonic generation (SHG and THG) with theoretical models, optical kerr effect (OKE), organic materials required for NLO, NLO applications), ***light amplification*** with the different related processes (laser, amplified spontaneous emission (ASE), random lasers (RL), Distributed feedback (DFB) lasers, organics dyes and amplification. This chapter part will be really a reference for future phD students, post-docs or trainees continuing in this field.

The second chapter corresponds to Anna Popczyk project itself and consists of several parts. The first one concerns:

-(1) the presentation of the molecular engineering *D-π-A* approach with the design of four families based on the benzo[b] thiophene as donor D and thiophene vinyl as a part of the conjugated bridge π. The family I (5 molecules) involves different acceptor A based on dicyano or indane-1,3-dione, while family II (6 molecules) corresponds to A acceptors with nitryl or NO_2 groups in ortho, meta ou para positions on phenyl groups. Family III (4 molecules) is composed of molecules with a substituted dimethylfuran related acceptors, and family IV (4 molecules) concerns molecules with benzo[b] thiophene as donor D and thiophene cyano-vinyl as a part of the conjugated bridge π with a substituted phenyl for the acceptor A. All molecules were obtained from the same aldehyde precursor **BT-O**, which will be used as molecule reference for all spectroscopic effects. Families I, III and IV molecules have been synthetized using a Knoevanagel procedure, while those of Family II were obtained with the Wittig-Horner method.

-(2) the presentation of experimental techniques: spectroscopy (absorption, luminescence, decay times, theoretical calculations, films preparation, NLO experiments (SHG, THG, OKE), light amplification (random lasing and DFB).

The next part deals with spectroscopic properties of these 20 molecules, according to their charge transfer strength, and then the nature of the different substituents. Absorption and emission (band position, quantum yield, stokes shift) properties, in solution, are discussed for each molecules family and rationalized by quantum calculations on charge transfer efficiency with modelisation of variations of electronic density between ground and first excited states, of the charge transfer distance, of the amount of the transferred charge and of the difference $\Delta\mu$ of the dipole moment between ground and first excited states. Solid state emission properties are also demonstrated, specifically aggregation induced emission effect (AIE) for families I and IV, while crystal fluorescence is also observed for one molecule of Family IV.

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NLO properties of these molecules in thin films are also presented. First of all, SHG and THG results in thin films are displayed for each molecules family. As expected, observations depend strongly on the nature of the acceptor group and on the efficiency of the charge transfer. As a second order process, SHG is closely related to ordering and higher values of $\chi^{(2)}$ susceptibilities are systematically obtained for *p-p* than *s-p* incident beam polarization. Anna Popczyk links $\chi^{(2)}$ and $\chi^{(3)}$ values to those of $\Delta\mu$. However, some exceptions are observed, such as molecule **BT-PhdiCN** with the highest value $\Delta\mu$ of 16 D but not the highest values of $\chi^{(2)}$ and $\chi^{(3)}$, displayed by molecule **BT-CNpNO$_2$**. Following SHG and THG, Anna Popczyk discusses OKE data, which cannot be related directly only in terms of $\Delta\mu$ values, but rather from Kramers-Krönig relation. The effect has been characterized, for each molecule, by several parameters: maximum of photoinduced birefringence, nonlinear refractive index, $\chi^{(3)}$ susceptibility, time constant of the static birefringence increase and decay; similar features have been also measured concerning dynamic birefringence. Family III, with molecule **BT-OCF**, seems to displays the best efficiency (maximum of photoinduced birefringence and dynamic OKE). This part ends with laser amplification tests. RL position bands depends strongly on the structure of the molecule (RL could be observed from the UV/blue to NIR depending on the charge transfer efficiency within the four families of molecules); furthermore, for molecules with high $\Delta\mu$ values, RL position could be tuned with the polarity of the host matrix. For almost molecules, the stimulated emission was obtained with a threshold lower than 1 mJ cm^{-2}.
The last part of this 2nd Chapter concerns the use of these molecules in the view of applications, based on effects described above. The first targeted application consider these molecules as possible sensors. For that, **BT-pNO$_2$** and **BT-PhdiCN** have been selected, due to their strong solvatochromism properties (significant shift of emission could be obtained from the blue to the green and from the green to the red ranges for **BT-pNo$_2$** and **BT-PhdiCN** respectively). Both molecules exhibit different behaviours with respect to solvent polarity: variations of emission with solvent polarity fit in agreement with dipolar interactions between solvent and dye for **BT-PhdiCN,** while hydrogen bonds and probe-probe interactions are favored for **BT-pNO$_2$**. A strong decrease of the emission intensity has been detected in presence of water or alcohols for **BT-pNO$_2$**, with a detection limit of 59 ppm in THF. Very interestingly, the emission change in presence of CN^- or OH^- anions have deeply studied for **BT-PhdiCN**: the appearance of a new band at higher energy leading to white emission at equilibrium, the following by NMR indicating the disappearance of the initial compound. This study allowed to show that **BT-PhdiCN** could be used as a CN^- or OH^- probe, which are toxic anions for environment, and this with a detection limit 0.0131 and 0.0025 µM respectively. DFB was also used by Anna Popczyk for the design of NIR organic solid state lasers (OSSL). **BT-TCF** and **BT-IsdiCN** in PPMA, selected for their NIR emission, led to a very broaly tunable NIR lasing effect (705-755 and 756-855 nm respectively) with a full width at half maximum varying from 0.15 to 0.50 nm, and a very promising energy threshold of 10 µJ cm^{-2}.

In conclusion, the very broad research performed by Anna Popczyk is displayed in a clearly written and well documented manuscript, reflecting her very good knowledge of the field. This typical multidisciplinary work is very dense (synthesis of 20 final original functional molecules, even though it did not correspond to Anna Popczyk initial expertise, and their numerous characterizations by NMR, optical spectroscopy, NLO, lasing and use in several applications). This work will arouse, undoubtedly, a high interest within international community, from a fundamental point of view, but also in terms of applications because it clearly opens up opportunities and prospects, specifically in the field of NIR OSSL useful in bio-imaging. This thesis already gave rise to four papers with high international impacts (*Nanomaterials, New Journal of Chemistry* and *Dyes and Pigments*). It is obvious that futher will be published in a next future.
This work, at the interface with several fields, allowed Anna Popczyk to acquire very broad skills, from organic chemistry to spectroscopy and physics. This represents a huge advantage a her future career.

All these considerations led me to give a very favorable opinion for Anna Popczyk oral defense in Wroclaw University of Science and Technology on December 9th 2021, in view of the obtention of the Docteur degree of Angers University.

Lyon, le 24 Novembre 2021

C. Andraud