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Report on the PhD dissertation of Mrs Paola Zimmermann-Crocomo

Mrs. Paola Zimmermann-Crocomo presents a PhD work on the photochemical and photophysical study and analysis, of various families of organic molecules, prepared by two groups of coworkers of Pr P. Data, and presenting original light emission characteristics. The properties aimed at with these molecules were centered on, while not only, Thermally Activated Delayed Fluorescence, also abbreviated as TADF. TADF in organic molecules begins to be well documented, but is nevertheless much less common than classical fluorescence, sometimes designated by prompt fluorescence (PF). It requires a specific synthetic approach which has been undertaken from several collaborative works. Alongside with the study of several families of new molecules, Mrs. Zimmermann-Crocomo describes the elaboration of some emitting devices based on these molecules.

After a short general introduction, the candidate starts by an introductory chapter detailing precisely the theoretical background into which her study is inscribed. The bases of molecular photophysics are recalled in a first general section. Then, the fundamental characteristics of Light Emitting Devices (LEDs) are given, the singlet and triplet natures of emitters is recalled, insisting especially on the possible S1/T1 interconversion, which is the basis of TADF. The importance of S/T interconversion is particularly important in such devices, since it is well known that, when excited states are created from electrical charges injection, only one singlet charge pair out of four is created (clear explanations with illustrating schemes are given on this precise point). The manuscript recalls that this situation considerably limits the emission yields, when the emission is based on fluorescence only and when in addition no S/T interconversion is possible, as it is frequently the case in organic molecules. Then, a special section is devoted to the description and understanding of the TADF process. A clear account of the four main partners of the emission, ¹LE, ³LE, ¹CT and ³CT is provided, followed by the description of the situations triggering the existence of fluorescence from a local state, a charge transfer state, or phosphorescence. Finally, an interesting and documented discussion is devoted to how to obtain TADF in purely organic molecules, the central subject of the work.

The rest of the introductory section is devoted to the description of the techniques that allow to identify, and further quantify, the different emission processes (PF, TADF, LTP and RTP). Successively are described the solvent polarity effects (solvatochromism), UV-vis absorption spectroscopy and different types of time-resolved emission spectroscopies and

finally electrochemistry and related spectroelectrochemistry. Also are discussed their uses in measuring the different energy levels existing in the molecules and implicated in their subsequent behavior. This introductory part is well written, quite inclusive and provides a complete theoretical framework for the interpretation of the following research work. Also is given along a detailed experimental part.

The rest of the manuscript is devoted to the description and analysis of the emission behavior of four different families of purely organic molecules, designed as to let appear TADF activity.

Chapter 4 treats with two different molecules, labeled A and B, who present exactly the same chromophoric units, a naphthalimide electron poor moiety conjugated with a carbazole donor unit attached on the para positions of one of the imide carbonyl groups. The only difference between molecules A and B is the addition of an extra bond between the carbazole and the other para position of the imide (in molecule B), which has the consequence to completely planarize the whole system. As it could be expected, the electrochemistry of the two molecules shows a drastic effect on the oxidation potentials (linked to the HOMO level) while a minor one on the reduction potentials (linked to the LUMO levels). This type of behavior has also been noticed with other systems, and shows that the LUMO is more localized on the attractor and less sensitive to conjugation. This demonstrates a smaller bandgap in the more conjugated molecule, as initially expected. The spectroscopic study corroborates roughly the results of the electrochemical study. Interestingly, there are little spectroscopic variations observed during the oxidation of both molecules. While the cation-radical (CR) of A is strictly unchanged, the CR of B displays a small change in the near UV band. The EPR study has been also effected and shows the rising of the spin signal upon oxidation as it could be expected. A detailed and well-done spectroscopic study is then presented. It demonstrates that the “weakly conjugated” A compound, because of the fact a noticeable part of the fluorescence comes out a charge-transfer state (ICT), indeed displays some TADF, because of its sensitivity to oxygen and its solvatochromism, among others. On the other hand, B, despite a very small energy difference between the singlet and triplet state, does not exhibit any TADF, due to its fully conjugated structure which forbids the existence of an emitting ICT. The study is indeed well done, my only regret being that no quantum yield measurement is given; that would have been interesting to know, especially in the case where A would have displayed a more efficient emission because of TADF.

The chapter 5 takes on a similar approach with another family of molecules, the dibenzophenazine type TADF emitters. These new molecules were already published in collaboration between two groups, partners of Pr Data's group, resp. Pr Monkman and Pr Takeda's groups. Actually these molecules were a coherent family, built from an invariable attracting dibenzophenazine core, substituted by a series of various donors (phenothiazines, carbazoles, etc...) and with a bent structure. A particular feature of these molecules is that some of them are able to polymerize, thus providing a double information: 1) How do polymer behave, and in a related way, 2) What is the incidence on devices of the photochemically induced coupling of active monomers upon long-time cell functioning. Actually a new molecule 5, featuring unsubstituted carbazoles instead of the more common tert-Bu substituted ones, was added for comparison sake. Again a comprehensive study of all

the family, electrochemical, and spectroscopic has been performed, putting in light the occurrence of TADF, and also pointing out the similarities and differences among the different molecules. A specific study has been performed on the derived polymers when a specific compound was able to polymerize upon electrooxidation. The studies in this chapter are extremely complete and represent a large amount of work. All UV-Vis, EPR, emission (PF, TADF, RTP, etc), electrochromism, have been performed both on all monomers and polymers, should they were obtainable. While the electrochromism results were a bit disappointing, on the other hand, the LEDs exhibited nice performances, including 14% for the new compound 5. This indicates the important future of this family of molecules, which probably can still be optimized to increase the devices' performances.

The following chapter 6 treats with two iminostilbene and iminodibenzyl derivatives, of ADA type, where the attractor is again of the dibenzophenazine type, while fused here. The difference between the two donors is that one is fully conjugated (the stilbene), used in molecule 9b, while in the other molecule 9a, a non-conjugated ethyl-bridged diphenylamine is used instead. While the family here resembles the previous (ch. 5) one, on the other hand the idea is more like the approach in ch. 4, to analyze how slightly changing the conjugation in the donor part can affect the spectroscopic properties of very similar molecules otherwise. This shorter chapter starts with an electrochemical study, which shows that as often with molecules analogous to triphenyl amines, electrodimmerization, or electropolymerisation is observed. However, the two issues are different, since in one case (the non-conjugated bridge) a real conducting polymer is observed, while in the second case, the reaction probably stops at the dimer stage. However, on the ground of the EPR and spectroscopy, the two compounds show much less difference than the ones in chapter 4. The emission behavior is relatively complex in both cases, but actually according to the conditions (temperature, polarity of the matrix), PF, TADF, LTP, RTP and even TTA can be observed with both compounds; however, in both cases, emission from the CT state was not seen or a very minor process. Therefore, the main differences are the relative importance and the range of occurrence of the different behaviors. Altogether, this is a nice and very complete. study, despite the results are less striking than in chapter 4. While conscious of the lesser expectations with these molecules, devices were tested, but the yields were much lower than with the previous series, the authors attributing correctly the fact to the low TADF occurrence.

The last chapter 7, in the reviewer's opinion the most interesting one (not surprisingly, it triggered an accepted article in *Angewandte Chemie*), treats with curved polycyclic aromatic hydrocarbons (PAH) featuring a central nitrogen atom. Already the N-including PAHs are intrinsically very interesting molecules, and this is even increased when their donor character is reinforced by a central nitrogen atom. The idea in this part of the work is to create fused with pyrazine attractors, completely conjugated with the curved PAH. The PAH remains always the same (no name given, but it is a kind of locked-in triphenylamine with internal C-C bonds) fused with various superstructured pyrazines, featuring (at one exception, the dicyano derivative 10f) an additional fused phenyl ring (thus transforming the pyrazine into a quinoxaline) with various attractors. The study is performed following the usual plan, electrochemistry, spectroscopy, time-resolved spectroscopy and finally devices construction. Very interestingly, all compounds feature TADF, and most of them successively PF, TADF and finally RTP, which make them very interesting compounds. Two of them (10d and 10f,

the dicyano substituted one) display triplet-singlet inversion like heptazines, and one (10b, the one with a diazaanthracene) displays a null triplet-singlet level difference.

Given their outstanding properties, all molecules were used to build up emitting devices. The results range between 11.5 % and 3.5 % (but this latter value for a molecule working on a RTP mode). These results are honorable, while a little bit lower than expectations knowing the spectroscopy. However, it demonstrates that these new curved PAHs are indeed a very promising family for future research.

Curiously enough, there is no general conclusion that could have been the occasion to make a point on the advantages and drawbacks of all the families of molecules examined, and also discriminate to which extent conjugation between the attracting and donating groups is, or not, favorable to the occurrence of TADF in organic conjugated molecules. However, this a really important and remarkable work, clearly written and well organized, and of course I recommend without reserves its acceptance for receiving the title of Doctor from the Silesian University of Technology.

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