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Please find herein, a report concerning the doctoral thesis manuscript of Mrs Michaela FECKOVÁ entitled *Matériaux luminescents hétérocycliques organiques et organométalliques: vers des applications OLEDs* in order to graduate with a doctoral degree from the Université de Rennes 1 and the University of Pardubice. The manuscript is 184 pages long and divided into six chapters, two of which are dealing with literature aspects (chapters 1 and 2), followed by three chapters (chapters 3-5) detailing original research projects and a final chapter (chapter 6) gathering synthetic protocols and characterization.
This rich manuscript details the development of an important number of fluorophores and gives an overall impression of excellent scientific integrity and maturity.
I will summarize below the main aspects of each chapter.

Chapter 1 aims at introducing the reader with the main aspects and notions of molecular luminescence, summarized in a classical but always useful Perrin-Jablonski diagram. In particular, Mrs Fecková details the electronic phenomena at the origin of luminescence in molecular scaffolds and the various dynamic processes of the excited-state which can influence these phenomena. Characteristic parameters involved in photophysical studies such photoluminescent quantum yields, excited-state lifetime or radiative/non-radiative deactivation constants are clearly explained and detailed. A strong emphasis is placed on the description of spin-orbit coupling occurring in fluorophores and its beneficial utilization for the possibility to reach spin-forbidden phosphorescence emission. This extended development on long-lived luminescence is particularly interesting and provides indispensable tools to contextualize the research projects developed in later chapters of this manuscript. Mrs Fecková carries on her introduction by thoroughly explaining the various parameters which have to be taken into consideration when one needs to establish structure-properties relationships. Electronic factors, length of π-conjugated linkers and two-photon absorption capacity are all detailed and placed in perspective with the goal to construct optimized luminescent materials. Environmental effects such as solvatation, pH or viscosity are also important parameters and are relevantly pointed out in the introduction by the author. Such data are indeed extremely useful in order to target valuable applications such as those developed herein. In this context, several classes of organic fluorophores reported in the literature are described such as coumarins, cyanines or boron complexes. This part, relatively short (1 page) could have been extended by detailing notably the main synthetic pathways and more reviews references would have been useful. Mrs Fecková chose to continue the chapter with a whole second part devoted to the OLED device explaining the structure, working principle, characteristics with a notable emphasis on the different types of OLED. This memo is particularly appreciated since the insertion of her luminescent probes in optoelectronic devices such as OLED is pointed out by Mrs Fecková as one of the main targeted applications. Overall, this introduction is extremely pleasant to read, scientifically thorough and gives a brief but much needed overview of the chemistry, photophysics and applications of luminescent molecular materials.

Chapter 2 is a second introductive chapter devoted to the description of the pyridimine heterocycle, a molecular ring Mrs Fecková derivatized and studied throughout her doctoral work, along with its insertion in the various luminescent materials reported in the literature with an emphasis in the construction of OLED. The physical properties (pKa, aromaticity index) of the pyrimidine ring are first nicely recalled in the perspective of other nitrogenated analogs including pyridine. An extensive review of the reported push-pull fluorophores incorporating one or two pyrimidine derivatives as electron-withdrawing groups is then presented. It is convenient for the reader to see the two-photon absorption data for each dye, in the figures but it would have been also nice to distinguish at first glance from the dyes previously developed in the laboratory of Mrs Fecková from dyes reported elsewhere. The synthetic approach of pyrimidine derivatives is briefly overviewed and should have probably been detailed a little further through examples since synthetic organic chemistry is at the heart of the research presented in this manuscript. Nevertheless, it is worth noting that each described pyrimidine derivative is closely associated with its potential application for polarity detection, ions detection, bioimaging or explosives detection with colorful illustrative figures highlighting the strong emission intensity stemming from these dyes. A special emphasis is placed on the possibility to engineer white emission from a single pyrimidine-based dye via a partial protonation process, a highly topical subject for the fabrication of white OLED. Finally, Mrs Fecková lists the reported examples of pyrimidine-based materials for OLED engineering and the corresponding performance in the device. This last part of chapter 2 is very instructive and nicely contributes to the contextualization of the original research developed in later chapters.

Chapter 3 consists in the synthesis of a rich library of fluorescent compounds based on the pyrimidine core (23 dyes were prepared!) followed by a full structural, photophysical and theoretical characterization of the resulting probes. The synthesis part summarizes the reaction yields of the various styryl-extended branching functionalizations at the 2, 4 or 6 position of the heterocycle, either via Pd-catalyzed Suzuki-Miyaura cross-coupling reaction or Knoevenagel condensation. The results are clear and well-presented, although a global board of results might have been a little easier to read. The synthesis yields range from mild to good and it is sometimes difficult to know if they were optimized as some of them are quite surprising (for example, 231c (85%) vs. 232c (17%) vs. 232j (65%)). The crystal structure of molecule 232h provides insightful information about the conformation of the dye. It is very pleasant to observe that these dyes were also characterized by differential scanning calorimetry (DSC) to provide melting points and thermal decomposition temperatures. The main part of this chapter is devoted to the study of the photophysical properties. All compounds were studied in dichloromethane and the results presented in a board which makes the reading easier. I was surprised to see that the same concentrations were used for measuring absorption and emission, as fluorescence spectroscopy is far more sensitive and usually requires dilution. The optical data of the various compounds are then compared, depending on substitution (acceptor or donor, *i.e.* methoxy, aromatic amines) and on numbers of styryl-extended arms, which is relevant and provides a clear overview of the photophysical characteristics of this family of dyes. Some dyes, not many, are completely quenched which Mrs Fecková attributes to a TICT process, without always mentioning why some are more prone to this process than others. The dyes featuring an aromatic amine expectedly display strong fluorosolvatochromism; a process which is fully studied in Table 5. This study shows the full potential of these dyes to act as ICT probes, as a strong emission seems to be observed even in polar media. It would have helped the discussion if Mrs Fecková had calculated the quantum yields in the various solvents studied. One missing aspect in this study is the absence of discussion about the possible photoisomerization processes which are commonly observed in fluorophores bearing styryl substitution. Repeated scans in the UV-Vis spectra would have helped quantifying this process. Moreover, in excited-states possessing a charge transfer character, solvent polarity tends to strongly interfere with the photoisomerization process of styryl spacers, with stronger photoisomerization efficiency in apolar media. Here again, determination of the quantum yields might have shed some light on this process (or the absence

of thereof). Protonation studies, undertaken with different acids are particularly instructive in order to understand the photophysical processes underlying these dyes. Titrations left no doubt about the monoprotonation of pyrimidine in these conditions leading to the appearance of a red-shifted emission band. The branching effect was then nicely summarized by Mrs Fecková through relevant examples which clearly demonstrate her perspective and insight on her research. Collaboration works on time-resolved spectroscopy, TD-DFT and two-photon absorption properties participate to the full characterization of this very interesting family of compounds. It is worth noting that Mrs Fecková's work detailed in this chapter was published in three recent articles in high-impact journals.

Chapter 4 dealt with the development 9,9-dimethylacridan substituted styryl-extended pyrimidine derivatives in order to tackle TADF emission and a subsequent insertion in OLED devices. After a brief but concise introduction, Mrs Fecková details the synthetic steps necessary to provide the final dyes. In the first step, I was surprised to observe that a Hartwig-Buchwald coupling between a secondary amine and a halogenated arene appeared to be completely unsuccessful. Questions about the synthetic protocol will be inevitably part of the discussion, as technical details are of upmost importance for the completion of such Pd-catalyzed cross-coupling reactions. Again, a full characterization was undertaken for the final dyes, including X-Rays and DSC curves. The photophysical properties studied in solution in a range of solvents with increasing polarity and in the solid-state revealed a strong fluorosolvatochromism behavior (ICT state). Moreover, emission spectra in the presence and absence of N_2 pointed out an increase of luminescence intensity under inert conditions for the more red-shifted band, indicative of long-lived luminescence. Unfortunately, excited-states dynamics studies showed biexponential days in the pico- and nanosecond range, inconsistent with the presence of expected long-lived TADF emission. TD-DFT calculations attempted to attribute the absence of TADF to the lack of oscillator strength. Owing to the presence of rotations in the ground state, some of these dyes also display aggregation-induced emission (AIE) which was evidenced in THF/water mixtures. Finally solid-state emission recorded on powders showed a nice fine-tuning of the emission bands. Mrs Fecková concluded this chapter by a summary of the various dyes studied. Here again, it was nice to see that this valuable work was recently published in a high impact factor journal.

Chapter 5 is reporting on platinum complexes involving a phenylpyrimidine ligand as solid-state emitters. A total of five complexes with substituted phenylpyrimidine as cyclometalated ligands, pyridine and chloride ion as ancillary ligands are reported. A X-Ray crystal structure confirmed a square-planar geometry along with a strong torsion angle between the plane of the pyridine ring and square-plane of the rest of the dye. Three dyes out of 5 were completely quenched in solution in DCM, even after N_2 bubbling which is ascribed to the possible pyridine ring rotation. In the solid-state, however, a bright emission with structured spectra was observed for all dyes, as powders. A fine-tuning of the emission color, between green and red is observed, highlighting the luminescent versatility of these derivatives. Again, these experimental observations were rationalized with TD-DFT calculations. These platinum complexes were recently published in Eur. J. Inorg. Chem.

Mrs Fecková then concludes her manuscript by a general conclusion and perspectives on these pyrimidine derivatives. Remarkably, she highlights the fact that her doctoral work has already been published in 5 articles with an additional participation in 3 more articles, leading to an impressive number of 8 articles so far published on these results.

In conclusion, I believe that this doctoral work, at the interface of heterocyclic chemistry, crystallography, calculations and photophysical studies compiles an impressive amount of original dyes, all fully characterized and studied. I also would like to emphasize the clarity of the manuscript with a very

consequent and thorough experimental part. The references section is also very consistent with the current literature on the subject.
As a result, I think that this doctoral undoubtedly deserves that Mrs Fecková is awarded with the title of doctor in Chemistry from the Université de Rennes 1 and the University of Pardubice and I give a very favorable opinion to the defense, scheduled on June 17th.

Dr. Julien Massue

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