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Opinion

Pyrazolo [1,5-A] Pyrimidines an Interesting Scaffold for Optical Applications

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Opinion

Organic fluorescent compounds are playing and will play an important role in scientific research in the next decades owing to their potential technological applications in the fields of chemo sensors, biological imaging, and optical devices [1]. With hundreds of metal-free dyes published every year an immediate question arises: is there any room for new organic fluorophores? To find an appropriate answer, we should analyze the present and past of organic fluorophores. On one hand, conventional organic fluorophores like pyrene, anthracene, or perylene are essentially non-fluorescent in the solid-state, which limits their usage in practical applications. On the other hand, more complex and modern organic dyes such as BODIPY, Rhodamine, or coumarin, to name a few, with exceptional optical properties both in solution and solid-state lack of good sustainable performance, with expensive manufacture processes and high amounts of wastes release during their production (Figure 1). Consequently, the answer to the above question is yes, as modern society we really need better fluorophores and thus, it is highly desirable to find modern alternatives that combine excellent photophysical performance with low-cost and efficient synthetic approaches. In this context, many reasons allow us to think that pyrazolo[1,5-a] pyrimidines, well-known for their wide applications in medicinal chemistry, emerge also as an important alternative for optical applications due to their proven synthetic versatility [1].

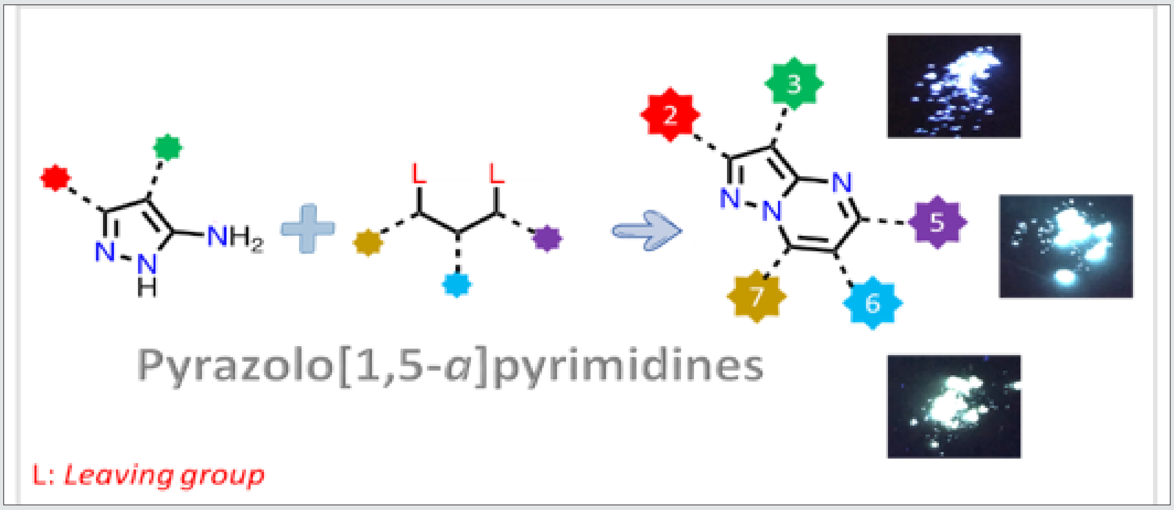

Figure 1:

From theoretical and crystallographic studies, the structure of pyrazolo[1,5-a] pyrimidines (PPs) have been found as a rigid and highly planar nucleus, vital features for optoelectronic applications. Moreover, the electronic communication with substituent on their periphery depends on the position and the bulky and/or electronic nature of the group attached. Thus, photophysical properties can be tuned from highly efficient fluorescent compounds in solution by using electron donating groups at position 7 to solid-state high emitters with bulky substituents in the same position [2]. Noticeable, most of the raw materials needed to produce pyrazolo[1,5-a] pyrimidines are non-expensive and commercially available compounds: amino pyrazoles, aldehydes, acetophenones, dimethylformamide-dimethyl acetal (DMF-DMA), β-dicarbonyl compounds or β-ketonitriles. Moreover, structural diversity in this fused pyrazole can be accomplished during their synthesis or via post-functionalization strategies. In general, the synthetic pathways involve a cyclocondensation reaction between an aminopyrazole with a 1,3-biselectrophilic system, in the absence of any metal catalyst, with good overall yields. Interestingly, the π-excedent pyrazolic ring in PPs is susceptible to electrophiles (position 3) while the π-deficient pyrimidine moiety is attracted to nucleophiles (positions 5 and 3). As a result, aromatic substitution reactions are frequent that allows further functional group introduction through well-known protocols like nitration ($-NO_2$), formylation (-CHO), halogenation (F, Cl, Br, or I), amination or coupling reactions. Therefore, a huge number of functional groups combinations with interesting biological and/or optical properties/applications can be synthesized starting from relatively simple raw materials.

Attractive photophysical properties such as good absorption coefficients (from 2001 to 39000 M^{-1} cm^{-1}), quantum yields as high as 98% in solution, and 63% at solid-state, excellent photostability, and absorption and emission wavelength tunable with the substituent nature in the periphery of the heterocyclic core, indicate that interesting set of applications can be formulated for this fluorophore. However, and for the best of our knowledge, just a few examples have been reported for the optical application of these compounds. For example, professor's Jian Feng Ge group in Suzhou (China) use a pyrazolo[1,5-a] pyrimidine-triphenylamine hybrid system to study the lipid content in cancer cells, thanks to their environment sensitive emission properties [3]. The same principle was used in our research group to propose a preliminary detection of water in organic solvents. Furthermore, we combined pyrazolo[1,5-a] pyrimidine with two cyanide acceptor groups at position 3, allowing the detection of this toxic anion (CN^-) by using UV-Vis and fluorescence techniques. In comparison with some other organic compounds regularly used for optical applications, the pyrazolo[1,5-a] pyrimidines have shown superior photostability, lower raw-materials cost per gram, tunable emission intensities in solution and/or solid-state, and higher reaction mass efficiency (lower waste generation). Therefore, we hope these interesting family of compounds will be useful alternatives for optical materials in non-linear optics, organic light emitting devices (OLEDs), organic solar cells, and chemo sensors field. By the time, we are working on a variety of applications related to other interesting substrates and are very excited about the results [3].

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