

Improved synthesis of tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles a promising dye for organic electronic devices: An experimental and theoretical approach

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ABSTRACT

Pyrrolo-[3,2-*b*]pyrroles represent a class of promising materials for application in organic electronics with interesting optoelectronic properties and great synthesis versatility, but yields obtained from varied synthetic routes are still very low, hindering their effective application for industrial purposes. In this report, we present a method for the synthesis of tetraaryl-1,4-dihydropyrrolo-[3,2-*b*]pyrrole derivatives by multicomponent reactions employing niobium pentachloride as a catalyst. The optical characterization of the products is also presented. Electronic structure calculations were performed to help the interpretation of the synthesis process, as well as the optical properties of the systems. Excellent yields and low reaction times were obtained, indicating that NbCl₅ is an efficient catalyst for such systems. The products show promising properties for optoelectronic applications that can be adjusted by the choice of benzaldehyde derivatives used in the synthesis.

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1. Introduction

Heteropentalenes belong to a class of heterocyclic compounds with two fused pentagonal rings [1]. Derivatives with 10 π electrons are aromatic and have been studied due to their potential use in electronic devices, such as solar cells [2], transistors [3], and electrochromic devices [4,5]. Among the aromatic heteropentalenes, those most frequently studied are the thieno[3,2-*b*]thiophenes and thieno[3,2-*b*]pyrroles [3,4,6–12].

In this context, dihydropyrrolo-[3,2-*b*]pyrrole derivatives have gained increasing attention in recent years, mainly because of their high fluorescence quantum yields and significant two-photon absorption (2PA) cross-sections [13–15]. In addition, the pyrrolo[3,2-*b*]pyrrole structure has also been predicted as the most efficient electron donor among the 10 π electron systems, such as thieno[3,2-*b*]thiophene and thieno[3,2-*b*]pyrrole [16]. Regarding optical

properties, it has been shown that some azapentalene derivatives present very broad absorption spectra presenting colorations ranging from blue to red [17–19].

Some works also show that the tetraaryl-1,4-dihydropyrrolo-[3,2-*b*]pyrrole derivatives can be used as starting materials to synthesize other electron-rich structures, including pentaaryl- and hexaaryl-1,4-dihydropyrrolo-[3,2-*b*]pyrroles, diindolo[2,3-*b*:2',3'-*f*]pyrrolo[3,2-*b*]pyrroles, bis(areno)-1,4-dihydropyrrolo[3,2-*b*]pyrroles and π -expanded indolo[3,2-*b*]indoles [20–27]. Recently, the technological relevance of pyrrolo[3,2-*b*]pyrrole derivatives has been demonstrated in applications such as the halocarbon detection cartridges [28] and the organic resistive memory [29]. However, in the field of photoelectronics, the pyrrolo[3,2-*b*]pyrrole derivatives are not yet studied, but similar heteropentalenes such as thieno[3,2-*b*]thiophenes appear as dyes in dye-sensitized solar cells (DSSC) [30,31], as hole transporters in Perovskite solar cells (PSC) [32], in organic light emitting diodes (OLED) [33], organic light emitting transistors (OLET) [34], organic phototransistors (OPT) [35] and organic photovoltaic cells (OPV) [36].

Pyrrolo[3,2-*b*]pyrrole derivatives can be synthesized via

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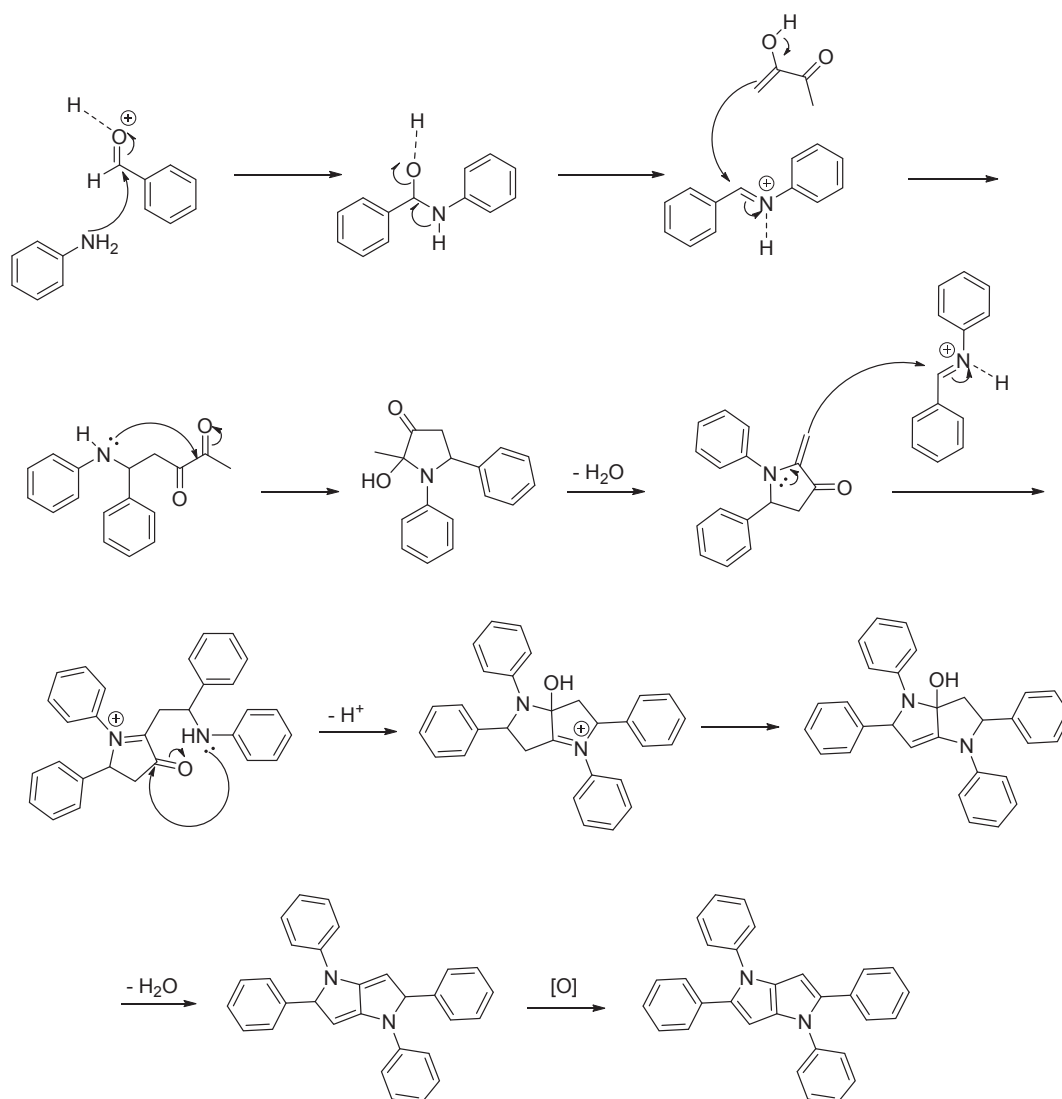
Knoevenagel reaction between pyrrolo-2-carboxialdehydes and ethyl azidoacetate, with a subsequent thermal cyclization [37]. Mukai and coworkers described the preparation of these materials in multiple steps, but showed low yields [38–40]. A new method for their preparation was reported in 2013, consisting of a domino reaction between an amine, an aldehyde and butane-2,3-dione in a 2:2:1 proportion and in glacial acetic acid at reflux. This reaction produces the desired tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrrole derivatives; however, low yields were still obtained (5–34%) [41]. A relevant improvement in this method was reported by the same research group in 2014, adding 10 mol% of *p*-toluene sulfonic acid as a catalyst to the reaction, which led to yields between 22 and 49% [42].

Janiga and coworkers suggest that the synthesis of tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrrole derivatives occurs by a Mannich multicomponent reaction (MCR), with *in situ* generation of a Schiff base, which suffers the attack of the enol form of the butane-2,3-dione, followed by a cyclization reaction to form an enamine intermediate. This enamine reacts with a second Schiff base, followed by another cyclization and finally an oxidation (Scheme 1) [41].

Based on such mechanistic proposal, it is possible to point out niobium pentachloride (NbCl_5) as a promising candidate to

promote the involved pentacomponent reactions. As a matter of fact, niobium pentachloride was the only Lewis acid capable of promoting the Mannich MCR between aniline, benzaldehyde and the acetophenone derivatives at room temperature with great yields and good reaction times highlighting its powerful catalytic properties [43].

NbCl_5 is highly electrophilic and therefore can act as a Lewis acid, catalyzing several organic reactions and leading to excellent yields [44–51]. In particular, good results have been obtained by using this material as catalyst in several MCRs [52–61]. In this context, in the present report, we evaluate the use of NbCl_5 as catalyst in the synthesis of tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrrole derivatives by the pentacomponent reaction involving benzaldehyde, aniline and β -diketone derivatives. Preliminary photophysical characterization of the obtained products was also conducted. Electronic structure calculations were carried out in order to interpret the results and also to propose derivatives with optimized opto-electronic properties.



Scheme 1. Mechanistic proposal for the synthesis of tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrrole derivatives.

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