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A new series of rod-like conjugated molecules with a pyrazine or a bipyrazine core. Synthesis and light emitting properties

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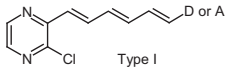
ABSTRACT

In this paper, we describe the synthesis of a wide range of new rod-like conjugated molecules with a pyrazine or a bipyrazine core connected to electron acceptor (A) or donor (D) groups through π-conjugated bridges as transmitters for the internal charge transfer (ICT). The key steps of the synthesis involve metallation and subsequent transmetallation of 2-chloropyrazine derivatives followed by Sonogashira or Negishi cross-coupling reactions. The bipyrazine core was obtained with a Stille cross-coupling reaction between the 2-chloro-6-tributylstannylpyrazine and the 2-chloro-6-iodopyrazine. Functionalization of the 6,6′-dichloro-2,2′-bipyrazine was performed by metallation, transmetallation and cross-coupling reactions. The light emitting properties of the so obtained molecules are then investigated in terms of absorption and emission spectra.

1. Introduction

Organic materials with extended π-extended conjugation along their backbone have received high interest owing to their applications in a wide range of electronic and optoelectronic devices.[1] Among them, rod-like chromophores with a planar and rigid π-conjugated system could be considered as molecular wires for electron and energy transfer[2] and also as materials in organic photo- and electro-luminescent devices. Another interest of such structures is their potential two-photon absorption (TPA) properties,[3] defined by their cross sections (σ_{TPA}), which could find applications in number of new areas, including the fluorescence imaging of biological samples,[4] optical limiting,[5] photodynamic therapy,[6] the three-dimensional optical data storage[7] and microfabrication.[8] The most extensively investigated structural motifs are donor-bridge-acceptor. The structure–property correlations of such chromophores reveal that the cross section σ_{TPA} increases with the donor/acceptor strength, conjugation length and planarity of the π-centre.[2b,c]

Previously, we have reported the synthesis of various linear dipolar D–π-A or quadripolar A–π-A compounds with a pyrazine moiety connected to a donor or and acceptor group through an oligoene chain as a bridge (type I).[9]



Type I

We describe herein the synthesis of various new conjugated compounds with a pyrazine or a bipyrazine core connected to electron acceptor (A) or donor (D) groups through π-conjugated bridges as transmitters for the internal charge transfer (ICT) (Scheme 1). These compounds with such a scaffold belong to dipolar structures with D–π-A systems (type II) or D–π-A–π-A systems (type III) and to quadrupolar structures with D–π-A–π-D system (type IV) where A is a π-deficient heterocycle unit (pyrazine or bipyrazine) (Scheme 1).

Compounds of type III with a D–π-A–π-A system could be compared to compounds of type I or II (D–π-A), allowing to appreciate for compounds of type III the structure–properties relationships due to the presence of a second arm at the C_6 position on the pyrazine ring as well as the nature of the π-conjugated linkers (alkene or alkyne units or polyenic chain). Chromophores of type IV have a centrosymmetric structure with a bipyrazine core and a D–π-A–π-D system, this kind of compounds is generally known to exhibit better two-photon activity (TPA) than the A–π-D–π-A systems.

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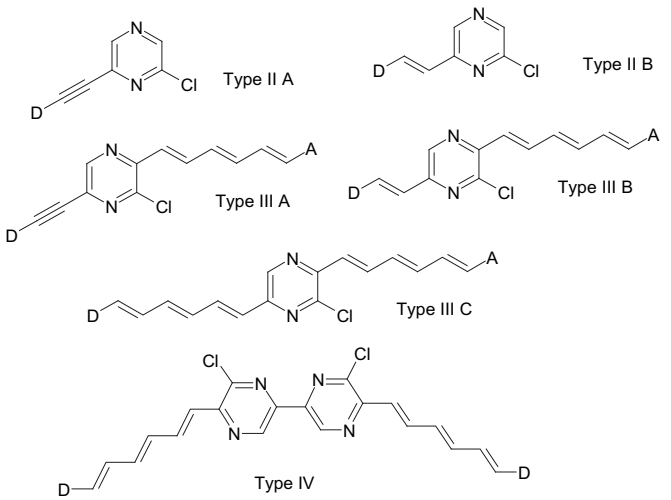


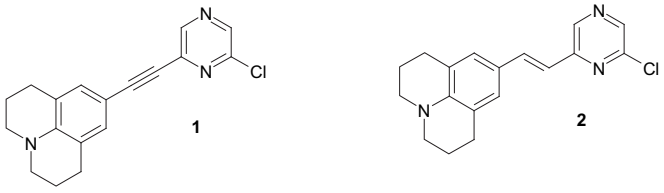
Scheme 1.

2. Results and discussion

2.1. Synthesis

It is well-known that amino groups are efficient electron-donating groups to induce large Stokes shifts in D–π-A systems because of internal charge transfer (ICT) states. Replacing dialkyl amino groups by a cyclic tetrahydroquinoline group would be one way to shift the absorption and emission to longer wavelengths.[10] For this reason we chose to introduce the julolidinyl group because of its high electron-releasing effect.

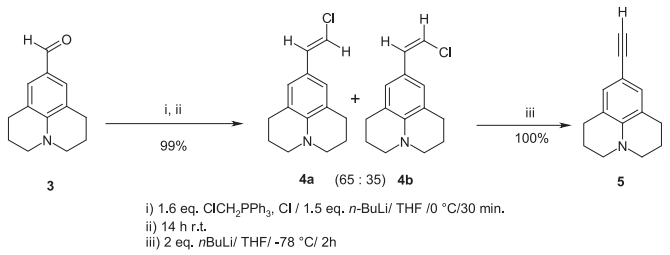
A preliminary synthetic way has been tested to introduce a julolidinylethynyl or a julolidinylvinyl group at the C_6 position of the 2-chloropyrazine (Scheme 2).



Scheme 2.

The 2-chloro-6-julolidinylethynylpyrazine **1** could be obtained either by a Sonogashira cross-coupling reaction between the julolidinylacetylene and the 2-chloro-6-iodopyrazine or by a Neghishi cross-coupling reaction with the organic zinc of the julolidinylacetylene and the 2-chloro-6-iodopyrazine. The two synthetic ways have been tested; the last one has given the better yield and is reported herein.

In a first time it was necessary to synthesize the julolidinylacetylene **5**. This compound was obtained in two steps from the formyljulolidine **3** as starting material, which was prepared by Vilsmeier reaction of julolidine[11] (Scheme 3).



i) 1.6 eq. $ClCH_2PPh_3$, Cl / 1.5 eq. *n*-BuLi/ THF /0 °C/30 min.
ii) 14 h r.t.
iii) 2 eq. *n*BuLi/ THF/ -78 °C/ 2h

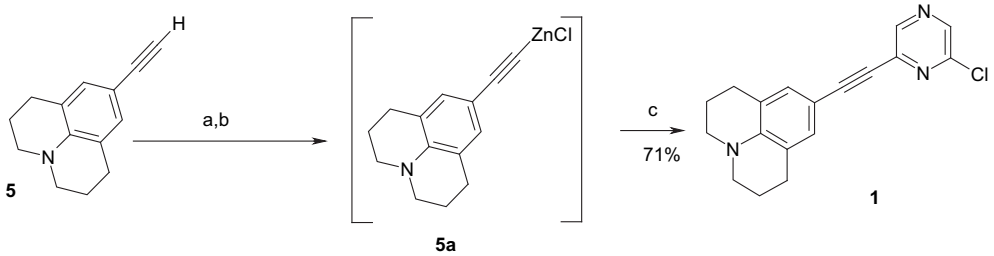
Scheme 3.

The formyljulolidine **3** was reacted with 1.6 equiv of chloromethyltriphenylphosphonium chloride according to the Wittig reaction conditions and with 1.5 equiv of *n*-butyllithium as base, leading to the 1-chloro-2-julolidinylethylenes **4a** and **4b** as a mixture of isomers *Z* and *E* (35:65) with a very good yield (99%). Further dehydrohalogenation carried out with *n*-butyllithium in THF at low temperature gave quantitatively the expected compound **5**.

The pyrazine derivative **1** was synthesized through the organo zinc intermediate **5a**, obtained by deprotonation of **5** with *n*-butyllithium followed by reaction with zinc chloride. The Negishi coupling reaction of **5a** with 2-chloro-6-iodopyrazine afforded **1** in 71% yield (Scheme 4).

Various attempts have been performed to synthesize compound **2**, the vinylene analogous of **1**. The Stille coupling reactions with stannylpyrazine and 1-chloro-2-julolidinylethylene have failed as well as catalytic reduction of **1** with the Lindlar catalyst. Another way has been tested using the hydrozirconation reaction with the Schwartz's reagent. The acetylenic compound **1** was reacted with 1.1 equiv of Cp_2ZrHCl in THF at room temperature, then a transmetallation of zirconium by zinc was performed by the action of zinc chloride and the Negishi reaction was carried out with 2-chloro-6-iodopyrazine. Under these conditions, the vinylene compound **2** was obtained in low yield (10%) besides the acetylenic compound **1** as major product (16%) (Scheme 5).

In order to appreciate the influence on the optical properties of the length and of the nature of the conjugated chain at the C_6 and C_3 positions of pyrazine ring, we have synthesized three other compounds of type IIIA or IIIB with a D–π-A–π-A system. These compounds were obtained from compounds **1** and **2** using metallation at the C_3 position, induced by the chlorine atom as *ortho*-directing group, followed by transmetallation and cross-coupling reactions (Scheme 6).



a) 1.2 eq. n-BuLi/THF/-78 °C/30 min
b) 3 eq. $ZnCl_2$/THF/-78 °C to r.t.
c) 1 eq. 2-chloro-6-iodopyrazine/ $Pd(PPh_3)_4$/ 5% mol/THF/r.t./4 h

Scheme 4.