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Bis- and tris(arylethynyl)pyrimidine oligomers: synthesis and light-emitting properties

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Abstract

In this contribution, we describe the synthesis of bis- and tris(arylethylnyl)pyrimidine oligomers using Sonogashira, Negishi and Suzuki cross-coupling reactions and starting from chloro or iodopyrimidines. When the arms of such banana-shaped and star-shaped molecules are substituted by electron-donating groups, interesting fluorescence properties were observed. The influence of the nature of the electron-donating groups was studied and a comparison with banana-shaped and star-shaped pyrimidine core molecules without ethynyl moities was carried out, showing that the triple bonds generally enable a red shift of the absorption and emission spectra and upgrade fluorescence properties in terms of quantum yield.

Keywords: Pyrimidine; Cross-coupling reactions; Fluorescence; Conjugation

1. Introduction

Organic materials with a π-conjugated backbone have received intensive research interest both in academic and industry due to their applications in a wide range of electronic and optoelectronic devices.[1] Among them, star-shaped and banana-shaped molecules have attracted a growing interest over recent years owing to their applications in various fields such as liquid crystalline,[2] light-emitting,[3] self assembling[4] and octupolar nonlinear optical[5] properties. Incorporation of a π-deficient heterocycle such as pyridine,[6] *s*-triazine,[7] pyrazine,[8] quinoxaline,[9] naphthyridine[10] or pyrimidine[11] in the centre of the backbone of such molecules leads to a strong enhancement of physical properties such as mesomorphism, fluorescence and solvatochromism. In π-conjugated materials, azaheterocycles such as pyrimidine can be used as the electron-deficient unit, its combination with conjugated character within the arms bearing donating groups would provide fluorescence with internal charge transfer (ICT) or twisted internal charge transfer (TICT) excited states upon electronic excitation with interesting solvatochromic properties. Such molecules can then be used as luminescent sensors in molecular biology and medical diagnostics, as active materials in self-assembled molecular devices.[12] The advantages of molecular fluorescence for sensing and switching are very important:[13] indeed they enable a high sensitivity of detection, an 'on–off' switchability, a subnanometer spatial resolution and a submillisecond temporal resolution.

Ethynyl moities added in the backbone lead to ethynyl aromatic/heteroaromatic systems which are versatile rigid molecules that have been successively exploited for the construction of a range of nanosized hydrocarbon molecular architectures such as rings, cages and dendritic macromolecules.[14] The main advantage of them compared to their arylenevinylene counterparts is the lack of possible *Z*/*E* isomerism and their higher stability.[15]

In a recent paper,[16] we have shown that some di- and triarylpyrimidines present good fluorescence properties with quantum yields reaching 0.72 and Stokes shifts generally superior to 6000 cm^{-1}. These fluorophores present also interesting fluorosolvatochromic properties and pH-sensibility.

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In order to extend the conjugation within the arms of the star-shaped and banana-shaped oligomers with the aim to improve their fluorescence properties, we have incorporated alkyne linkages between the pyrimidine central core and phenyl moieties. We report herein the synthesis of bis- and tris(arylethylnyl)-pyrimidine oligomers and their light-emitting properties. This study is a part of our work dedicated to the use of diazines as building blocks for the synthesis of new molecular materials.[17]

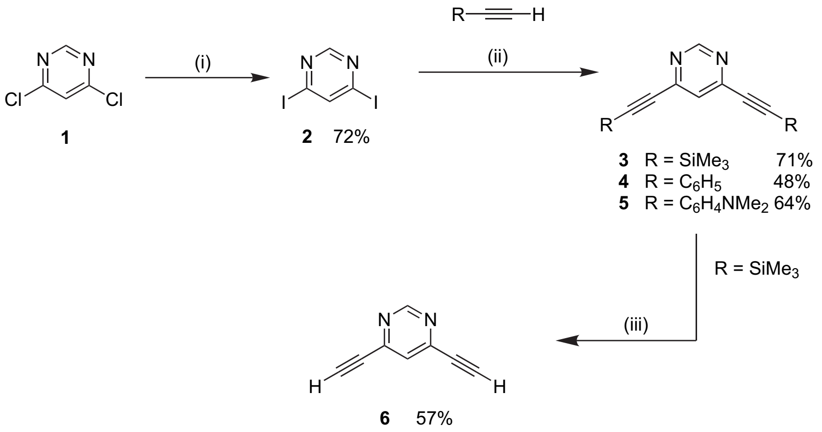
2. Results and discussion

2.1. Synthesis

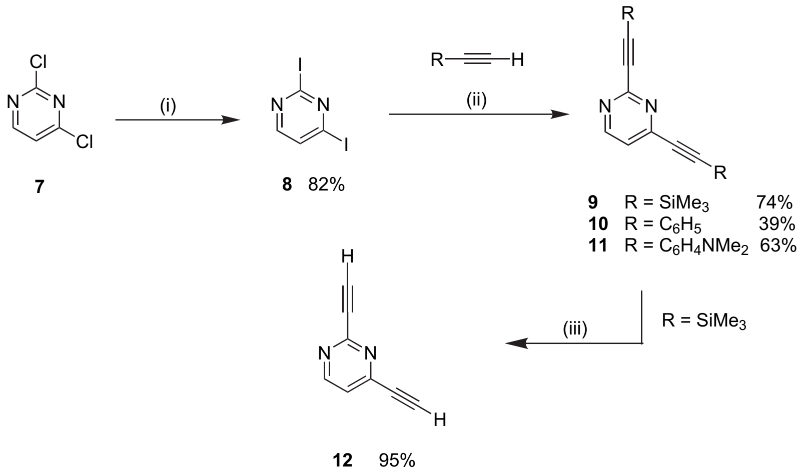
The Sonogashira cross-coupling reaction[18] is one of the most common method to introduce an ethynyl moiety on aryl compounds. The π-deficient character of the pyrimidine ring makes easier the oxidative addition of palladium on the chlorine–carbon bond,[19] allowing to carry out Sonogashira cross-coupling reactions with chloropyrimidines. However, the yields kept low,[20] and this latter coupling is generally performed with iodopyrimidines. First examples of the synthesis of diethynylpyrimidines were reported by Yamanaka and co-workers with medium yields.[21] Starting from 2,4-diiodopyrimidine and 4,6-diiodopyrimidine, easily obtained from chloro derivatives by nucleophilic substitutions,[22] we synthesized the expected dialkynylpyrimidines using this methodology. Dialkynylpyrimidines were then obtained with medium to good yields, when the alkyne used is trimethylsilylacetylene. Further cleavage of the trimethylsilyl groups with potassiun hydroxide in methanol led to compounds **6** and **12**, which could be used as building blocks for the synthesis of nanoarchitectures (Schemes 1 and 2).

The reactivity of 2,4,6-triiodopyrimidine **13** is efficient enough to allow its triarylation under the Suzuki cross-coupling conditions,[23] whereas reaction of **13** with 5 equiv of alkyne under Sonogashira conditions did not afford the expected trialkynylpyrimidines. In this latter case only tarry products were obtained probably due to the low stability of the triiodo derivative (Scheme 3).

An other well-known method to introduce ethynyl moieties on aryl compounds is the palladium-catalyzed Negishi cross-coupling reaction using alkynylzinc chlorides easily accessible from alkynyllithiums.[24] Recently, using this method, Tobe and co-workers[25] described the synthesis of triethynyltriazines starting from cyanuric chloride with good yields. However,



Scheme 1. (i) HI 57%, rt, 72 h; (ii) $PdCl_2(PPh_3)_2$/CuI, THF/NEt_3, rt, 15 h; (iii) KOH/MeOH, 15 min, rt.



Scheme 2. (i) HI 57%, rt, 2 h; (ii) $PdCl_2(PPh_3)_2$/CuI, THF/NEt_3, rt, 15 h; (iii) KOH/MeOH, 15 min, rt.