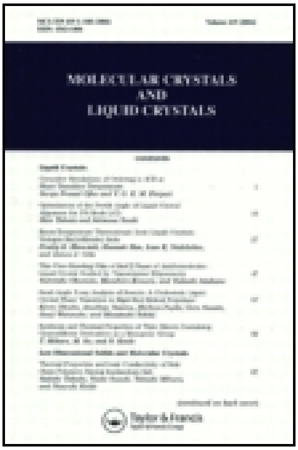

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Synthesis and Properties of Dipyridylcyclopentenes

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Synthesis and Properties of Dipyridylcyclopentenes

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A short and general route to the substituted dipyridylcyclopentenes was explored and several new compounds belonging to this new group of diarylethenes were synthesized. The study of their photochromic and thermochromic properties shows that the rate of the thermal ring opening is strongly dependent on the polarity of the solvent.

Keywords: diarylethene; photochromism; thermochromism

INTRODUCTION

Among photochromic materials a lot of attention is paid to the systems whose behaviour is responsive to more stimuli than just light. Dithienylethenes with pyridine substituents have been studied thoroughly by several groups. They have been used to demonstrate electronic communication through dithienylethene backbone [1], to construct supramolecular assemblies [2], and it was shown that their ring-closing reaction can be achieved electrochemically [3].

We have synthesized two basic representatives of the new group of diarylethenes in which the pyridine moieties are attached directly to the cyclopentene or perfluorocyclopentene ring (Fig. 1) [4]. As it was expected, these new switches have some unique properties arising from the presence of nitrogens as a proton and metal binding sites

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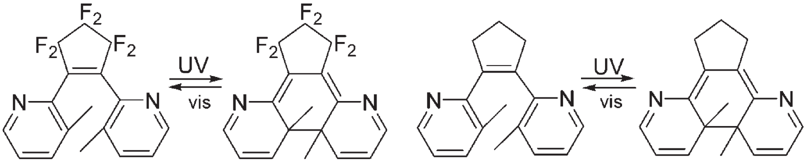


FIGURE 1 Basic dipyridylethene photochromic switches.

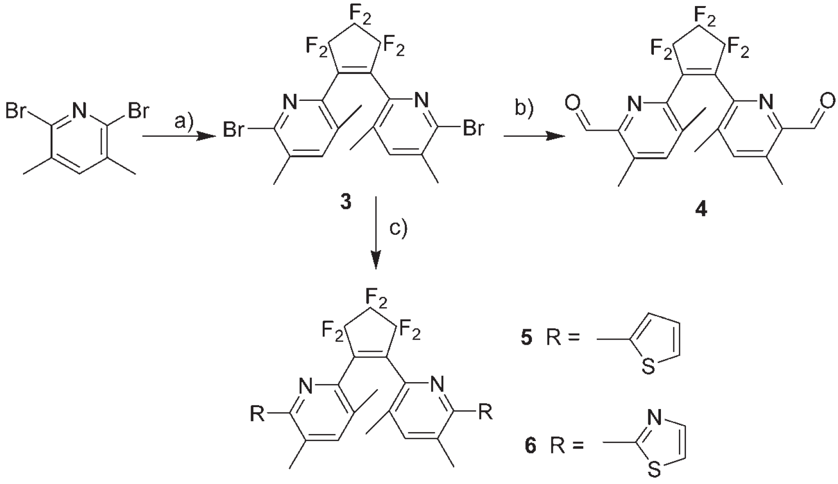
directly in the photochromic core. Not only do they show shift of the absorption maxima upon protonation but also gated photochromism when the protonated open form does not undergo the photochemical ring closing, whereas the ring opening reaction stays unaffected. Compound **2** can be gated also by presence of Cu(1+) ions creating 1:1 complex. To enlarge this group of photochromic switches, we were looking for the methods that would conveniently lead to substituted dipyridylcyclopentenes.

RESULTS AND DISCUSSION

The initial attempts to directly derivatize compounds **1** and **2** by ortholithiation with n-BuLi/N,N-dimethyaminoethanol [5] or orthohalogenation through pyridine N-oxides [6] failed. Therefore it was necessary to prepare dipyridylethene from precursors that already contained functional groups which were easy to substitute.

Dibromo substituted dipyridylethene **3** was prepared in 67% yield from the known 2,6-dibromo-3,5-dimethylpyridine [7]. It can be very conveniently converted into a variety of derivatives through halogen-metal exchange and a consequent reaction with electrophiles or through one of the many cross-coupling reactions involving arylhalides (Sch. 1). A disadvantage of this precursor is the presence of the methyl group in the ortho position to bromide, which may be a source of steric hindrance for bulkier substituents such as a phenyl group, pushing it out of the plane of the pyridine ring and disrupting the conjugation.

Dibromide **3** shows only limited photochromism and dialdehyde **4** is not photochromic at all. However, dipyridylethenes with electron rich substituents such as thiophene **5** and thiazole **6** perform very well. After irradiation with 313 nm UV light a new peak with the absorption maximum around 650 nm appears, indicating the presence of the closed form of the switch. The peak is extremely broad, covering almost the whole visible spectrum up to 850 nm (Fig. 2). However, both



a) i)n-BuLi, Et_2O, -78°C, ii) octafluorocyclopentene -78°C to room temp.
b) i)n-BuLi, Et_2O, -78°C ii)DMF -78°C to rt
c)2-(tri n-butytin)thiophene or 2-(tri n-butytin)thiazole, $Pd(PPh_3)_4$, CuI, toluene, reflux

SCHEME 1 Synthesis of substituted dipyridylcyclopentenes.

compounds **5** and **6** are thermochromic even at room temperature, a common feature for all dipyridylethenes.

By screening the photochromic reaction in various solvents only very weak solvatochromism (shift up to 10 nm) in the open as well

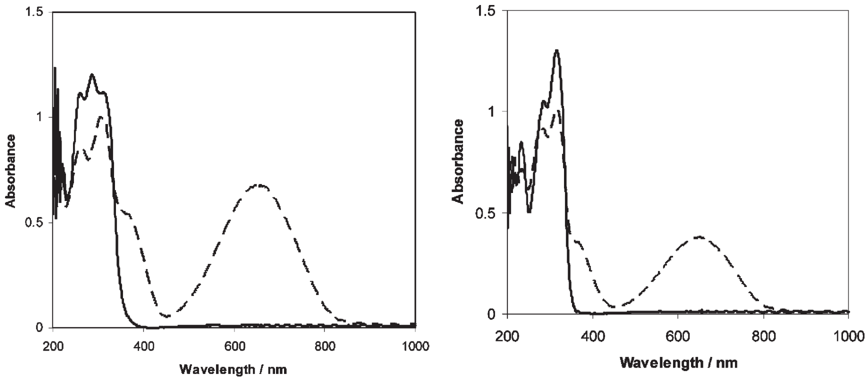


FIGURE 2 Absorption spectra of **5** and **6** in dichloromethane before (——) and after (----) irradiation with 313 nm light.

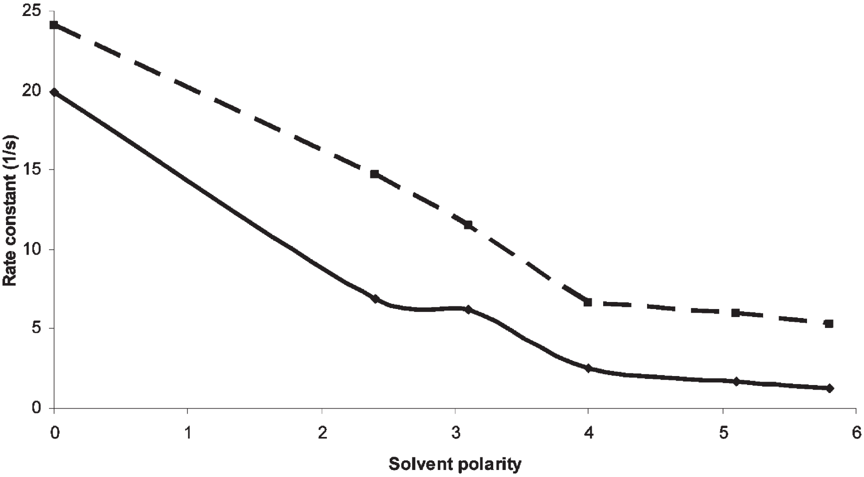


FIGURE 3 Solvent polarity dependent rate of thermochromic reaction of **5** (——)(rate constant multiplied by 10^4) and **6** (----)(rate constant multiplied by 10^3).

as in the closed form was observed, without any correlation to solvent polarity. Nevertheless, to our surprise, the thermochromic reaction occurred to be very solvent dependent (Fig. 3). The thermal ring-opening of dithienyl derivative **5** is as many as 20 times slower in acetonitrile than in hexane. To our knowledge, such a phenomenon has never been reported for diarylethenes, although it may lead to a valuable insight into the nature of the thermochromic ring-opening which is most probably thermally forbidden conrotary electrocyclic process.

CONCLUSIONS

Many substituted dipyridylethenes are accessible in just one step from the easily prepared precursor. Electron donating substituents are required to achieve good photochromic properties. Some of the prepared compounds show thermochromism which is dependent on the polarity of their environment.

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