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Journal of Photochemistry and Photobiology A: Chemistry 139 (2001) 1–4

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Spectroscopic properties of thiophene linked [2H]-chromenes

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Received 19 October 2000; received in revised form 21 October 2000; accepted 7 November 2000

Abstract

The influence of an oligothiophenic substituent upon the spectroscopic behaviour of chromenes is discussed. Fluorescence emission is observed for several compounds. The photochromism/fluorescence ratio depends on the polythiophenic chain length and on the substitution site on the chromene. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oligothiophenic [2H]-chromenes; Fluorescence emission; Photochromic systems; Molecular switches

1. Introduction

Organic materials such as photochromic compounds, whose structure and macroscopic properties can be controlled by light irradiation are presently an important field of interest [1–7]. Obviously, research in this area has increased significantly. Photochromic systems linked to a conducting material may have possible applications as optical switches in logic systems and light-modulators; recently, naphthopyrans (chromenes) have found applications related to materials undergoing such properties [8].

Let us consider a molecular system associating two conducting chains linked through a photochromic spacer. The photoinduced structural transformation between the colourless and coloured forms of the photochromic unit involves some modifications of polarity and π-conjugation, thus modifying the conducting or semiconducting properties of the material.

Naphthopyrans (chromenes) exhibit such properties and undergo an interesting photochromic behaviour, associated with a good fatigue resistance and a wide field of light absorption in the visible range [5,6,11].

The closed and open forms of a chromene are in equilibrium when a suitable light irradiation is applied (Scheme 1). When linked to a conducting material, such a system can possibly operate as a molecular switch.

Polythiophenes are well known for their conducting or semiconducting properties, and are almost inert towards water or oxygen; but these polymers present a very scarce solubility in organic solvents (above hexamer), and their chemical reactivity is consequently low [10,11].

Fundamentally, thiophene oligomers can be considered as a simplified model of polythiophenic chains. Garnier [9,13] has shown that short oligothiophenes (4–6 unities) display electronic properties similar to those of polymeric thiophenes, and preliminary encouraging studies concerning the conductivity of such materials were already performed [4,12,14].

According to the described model, we thus considered several systems including [2H]-chromenes linked to short thiophenic entities (Scheme 2). Avoiding the disadvantage of the insolubility of a polymer, we could study the spectroscopic behaviour, the photochromism and the potentiality as molecular switches of these thiophenic substituted [2H]-chromenes.

2. Materials and methods

The [2H]-chromenes linked to short thiophenic compounds were previously synthesised in our laboratory [15,16].

The absorption spectra were determined with a CARY 50 Varian spectrophotometer (2.0 nm spectral band pass) using 10^{-6} M solutions (THF, spectroscopic grade) of the chromenes. The absorption spectra of the open forms of

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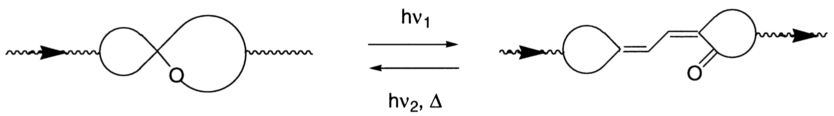
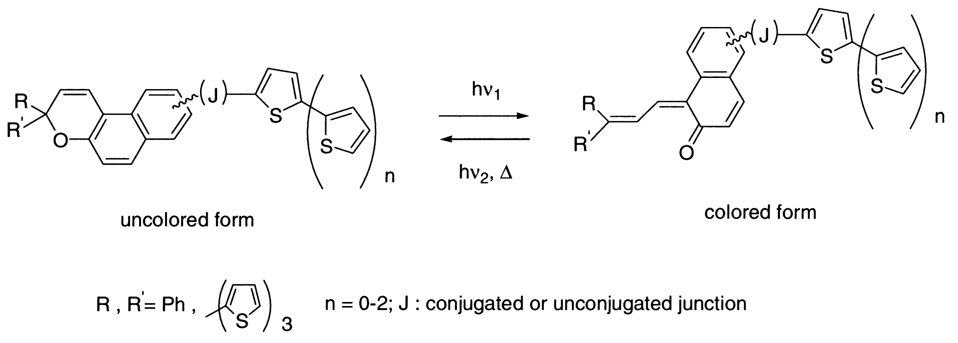
PII: S1010-6030(00)00410-X



Scheme 1.



Scheme 2.

the chromenes were obtained under continuous irradiation at the steady state, with a xenon lamp (Ushio type UXL-150SO/Oriel Instruments).

The fluorescence spectra were determined on an LS 50 Perkin–Elmer Spectrofluorimeter model. Photochromic compounds were diluted in THF of spectroscopic grade (UCB) for a concentration of 10^{-6} M.

The raw absorbances of the closed forms were corrected according to the same optical density ($\varepsilon \times C$) value for each compound, in order to compare their emission intensities.

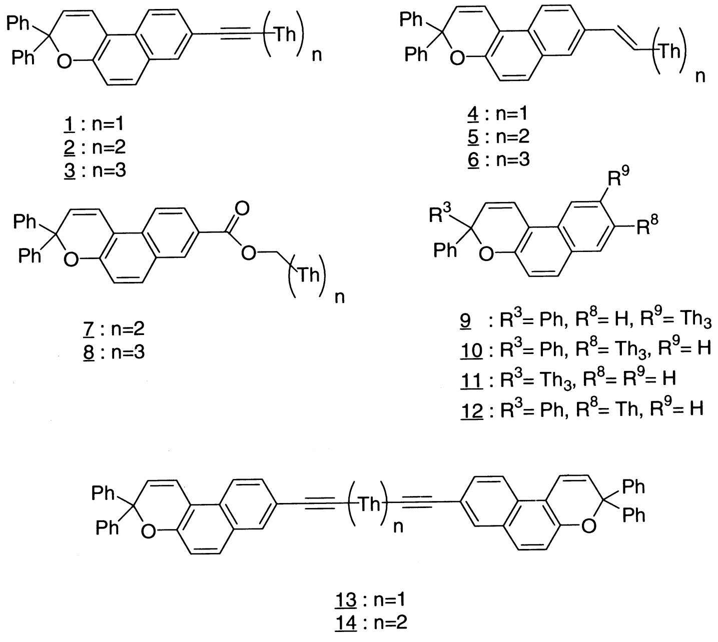
For the compound **11**, continuous UV irradiation during the fluorescence measurements were performed with a xenon lamp.

3. Results and discussion

The photochromic reaction, i.e., a reversible ring-opening of the pyranic ring, features the dissociation of the C(sp^3)–O bond (Scheme 1). As a matter of fact, a significant modification of the conducting properties of the system is directly dependent on its photochromism. In order to appreciate the efficiency of such a photochromic-conducting system, we first considered the influence of the thiophenic substituent upon the photochromism intensity of the chromenic group.

The studied chromenes were described in Scheme 3.

Compounds **3**, **6**, **9**, **10** include a conjugated terthiophen linked to the naphthalenic system. Such a thiophenic



Scheme 3.

Table 1
Spectroscopic data of thiophene substituted chromenes

Compound	Closed form λ max absorption (nm)	Open form λ max absorption (nm)	Relative intensity of photochromism A/A_{13}[a]	Closed form λ max emission (nm)	Relative intensity of emission I/I_6[b]
1	312, 338	470	0.44	–	0
2	345, 367	485	0.75	420, 440	0.29
3	410	490 very weak	0	455, 480	0.60
4	354	485	0.37	–	0
5	395	499	0.08	442, 465	0.86
6	273, 425	–	0	476, 507	1
7	322, 338	445	0.17	–	0
8	356	440	0.11	410, 435	0.09
9	397	–	0	456, 482	0.62
10	395	–	0	454, 480	0.30
11	360	528	0.39	417, 435, 465[c]	0.07, 0.03
12	319, 356	470	0.25	–	0
13	331, 378	474	1	425, 450	0.61
14	404	485	0.20	460, 485	0.91
15	–	–	0	405, 430	0.10

[a] The absorbance A_{13} of compound **13**, measured under flash photolysis conditions (toluene, $C = 2.5 \times 10^{-5}$ M, flash power 60 J, duration of flash 50 μs, 10 cm cell), has been taken as reference.

[b] Fluorescence emission intensities are related to 10^{-6} M THF solutions. The fluorescence intensity I_6 of compound **6** has been taken as reference.

[c] Fluorescence emission of the open form, measured under continuous irradiation.

oligomer is suitable as a conducting model; but all these compounds display a low photochromism and are highly fluorescent. This suggests that the absorbed energy induces the fluorescence of the terthiophenic substituent, instead of the ring opening of the chromene [17,18].

Chromenes **9** and **10**, including a terthiophenic substituent linked to positions 9 and 8, respectively, exhibit identical photochromism and fluorescence spectra.

In order to estimate the influence of an oligomeric thiophenic group, the spectroscopic data of other structures were considered (Table 1).

A monothiophenic substituent diversely linked to the position 8 of the naphthalenic system (compounds **1**, **4**, **12**) does not induce fluorescence emission, and these compounds were highly photochromic.

Compounds **2**, **5**, **8**, **11**, **13** were characterised by a fluorescent system constituted of three chromophoric components: one acetylenic link and a bithiophenic group, two acetylenic links and a monothiophenic group, a non-conjugated ester link and a terthiophenic group, or one ethylenic link and a bithiophenic group. All these chromenes exhibit medium photochromism and fluorescence efficiency.

Oligothiophenes are well known as highly electroactive systems [19]. Molecular calculations on HOMO and LUMO for the closed forms of the reference chromene and mono- or oligothiophene substituted chromenes were effected (AM1 Hamiltonian, AMPAC program [20]); the results show that the C–O bond cleavage in the singlet excited state is not significantly affected by the substituent linked to position 8, suggesting that the evolved colour is still due to a photochemical mechanism.

Otherwise, the same calculations show a charge transfer from the chromenic moiety and an increased electronic density for the sulphur atoms of the thiophenic group. It appears that when the link allows π-conjugation between the chromenic and thiophenic parts, the spectroscopic behaviour may be correlated to an electron charge transfer involving the photochromic and thiophenic parts of the molecule.

As a matter of fact, a bithiophenic substituent linked to the position 8 through an ester group (therefore, unconjugated with the naphthalenic system) does not induce fluorescence emission, and compound **7** is highly photochromic. Chromenes **13** and **14**, including a mono or bithiophenic spacer and two chromenic units, exhibit a weak photochromism and a fluorescence emission due to the conjugated bithiophenic group.

Let us consider the compounds **1**–**3** and **4**–**6**, respectively, according to the number of thiophenic units (*n* value, Scheme 3) of the linked group. The spectroscopic data show that the length of the oligomeric thiophenic substituent apparently controls the photochromism intensity and in some cases suppress the photochromism. Consequently, the fluorescence emission intensity of the closed form increases when the photochromism intensity decreases (compounds **2**, **3** and **5**, **6**).

The closed form of the compound **11** gathers the structural characteristics which prohibit the π-conjugation between the terthiophenic group and the naphthalenic system of the chromene framework, because the terthiophenic oligomer is linked to the chromenic C(sp^3) atom (position 3). Compound **11** is highly photochromic and slightly fluorescent, with the characteristic emission spectrum of terthiophen **15** itself [18].

Under continuous irradiation with a xenon lamp, the emission spectrum of the open form appears for compound **11** only, overlapped with the emission spectrum of the closed form. A bathochromic effect (30 nm) is observed for the fluorescence of the open form, obviously, due to the extended π-conjugation of the thiophenic chromophore. Such a modification is not observed with the other chromenes, suggesting that their open and closed forms exhibit the same emission spectra.

4. Conclusion

An oligomeric thiophenic substituent linked to the naphthalenic system strongly lowers the photochromism intensity. Chromenes **3**, **10**, **9**, **6** act rather as light converters instead of photochromic compounds.

Differently, the chromene **11** appears as an acceptable precursor for optical switches, insofar as a second thiophenic oligomer will be connected to the chromene; this possibility is actually studied in our laboratory.

Acknowledgements

The authors gratefully acknowledge Dr. J. Kister, ESA-CNRS 6171, University of Aix-Marseille III, for the kind access to the LS 50 Perkin–Elmer Spectrofluorimeter.

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