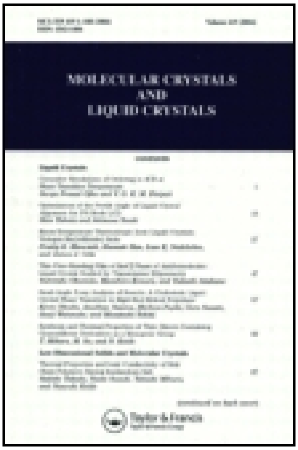

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Transient Absorption Investigation of the Photophysical Properties of Thiophene Linked [2H]-Chromenes

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Transient Absorption Investigation of the Photophysical Properties of Thiophene Linked *[2H]*-Chromenes

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The photophysical and photochemical properties of a bi-thiophene linked 2H-chromene are investigated by femtosecond and nanosecond transient absorption spectroscopy. The spectral characteristics and dynamics of the lowest excited singlet and triplet states are determined. The ring-opening reaction responsible for the photochromism is observed to occur in the S_1 *state with a time constant of about 150 ps in acetonitrile.*

Keywords: oligothiophenic *[2H]*-chromenes; photochromism; photophysical properties; transient absorption

INTRODUCTION

3,3′-diphenyl-3H-naphtho[2,1-*b*]pyrans (*[2H]*-chromenes) substituted in position 8 by thiophene oligomers via an acetylenic junction (shown below) have been recently synthesized in regard to their potential use

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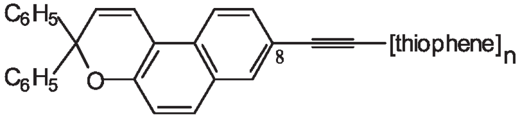


n = 0 - 3

in the elaboration of polythiophenes with photo-switchable optoelectronic properties [1]. In this family, photochromism proceeds via the cleavage of the spiro-carbon – oxygen single bond of the chromene moiety [2]. The reaction leads to a colored merocyanine form (open form). It has been observed previously that the photocolorability increases progressively as the length n of the oligomeric thiophenic substituent increases from 0 to 2 but the $n = 3$ compound does not show any colorability [3,4]. On the other hand, the fluorescence intensity of the closed form increases continuously from $n = 1$ to $n = 3$ [3]. In order to understand this apparently puzzling influence of the substituent length on the energy relaxation pathways and photochromism intensity, we have undertaken an investigation of the photophysical and photochemical properties of this family of compounds by transient absorption spectroscopy in the femtosecond to microsecond time domain. This technique has recently appeared very powerful in providing detailed information relative to the photochromism efficiency in the neighboring spironaphthoxazine family [5]. We present here some preliminary results concerning the bi-thiophene ($n = 2$) compound (named 8BT-C).

EXPERIMENTAL

Synthesis and purification of 3,3′-diphenyl-3H-naphtho[2,1-*b*]pyran substituted in position 8 by a bi-thiophene group via an acetylenic junction (8BT-C) was reported previously [4]. Acetonitrile and cyclohexane (Aldrich, spectrophotometric grade) were used as received. Femtosecond transient absorption measurements were performed on 2.5×10^{-4} M solutions circulating in a 2 mm thick flow cell, by using a pump-probe apparatus based on a Ti-Sapphire femtosecond laser system [6]. Pump pulses were tuned at 377 nm (100 fs, 1 kHz, 1.5 μJ). Spectra were recorded in the 400–800 nm range with a white light continuum probe set at the magic angle (54.7°) relative to the pump, and were corrected from GVD effects. The time resolution was better than 300 fs. The nanosecond transient absorption spectra were recorded in the 280–800 nm region using the 355 nm output of a Yag laser (10 ns, 1 mJ, 20 Hz) as pump excitation and a Xe flash lamp as the probe. Samples were contained in a quartz cell ($1 \times 1\,\mathrm{cm}^2$ section) at a concentration adjusted to get an OD value of ~1.0 at 355 nm. Solutions were degassed by bubbling N_2.

RESULTS AND DISCUSSION

Figures 1 and 2 (part A) show transient absorption spectra recorded in the 0.8–1000 ps and 1–64 μs time domains, respectively, following pulse excitation of 8BT-C in acetonitrile. Similar spectra were obtained in cyclohexane. The 0.8 ps spectrum shows a negative band at 425 nm, ascribed to stimulated emission ($S_1 \rightarrow S_0$ transition) as it matches the fluorescence spectrum of 8BT-C, and an absorption band at 588 nm. Both signals decaying concomitantly ($t_{1/2} \sim 150$ ps in acetonitrile), the 588 nm band can be ascribed to the S_1 state absorption ($S_1 \rightarrow S_n$ transition). The residual spectrum obtained after complete decay (1000 ps spectrum in Fig. 1) shows an absorption maximizing around 485 nm and a shoulder in the 550–650 nm region. This spectrum is comparable to that observed at 1 μs (Fig. 2A). The negative band lying below 400 nm in the 1 μs spectrum corresponds to the position of the ground state absorption of the closed form and is indicative of its depopulation upon excitation (bleaching signal). One observes in Figure 2A the complete

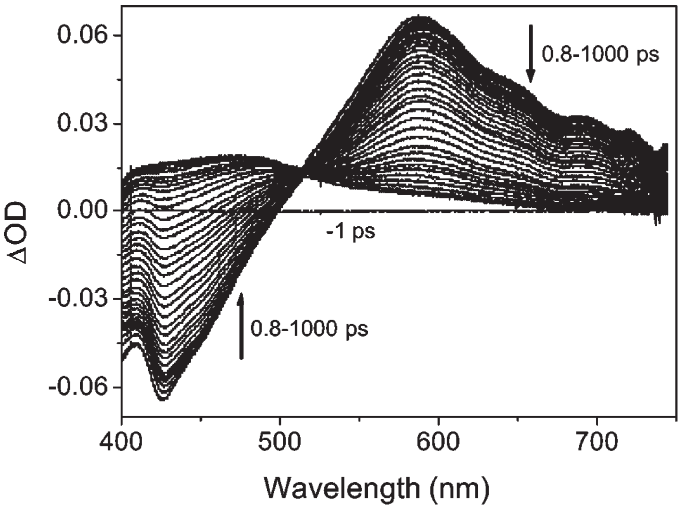


FIGURE 1 Transient absorption spectra of 8BT-C (2.5×10^{-4} M) in acetonitrile at different time delays after a 100 fs pulse excitation at 377 nm.

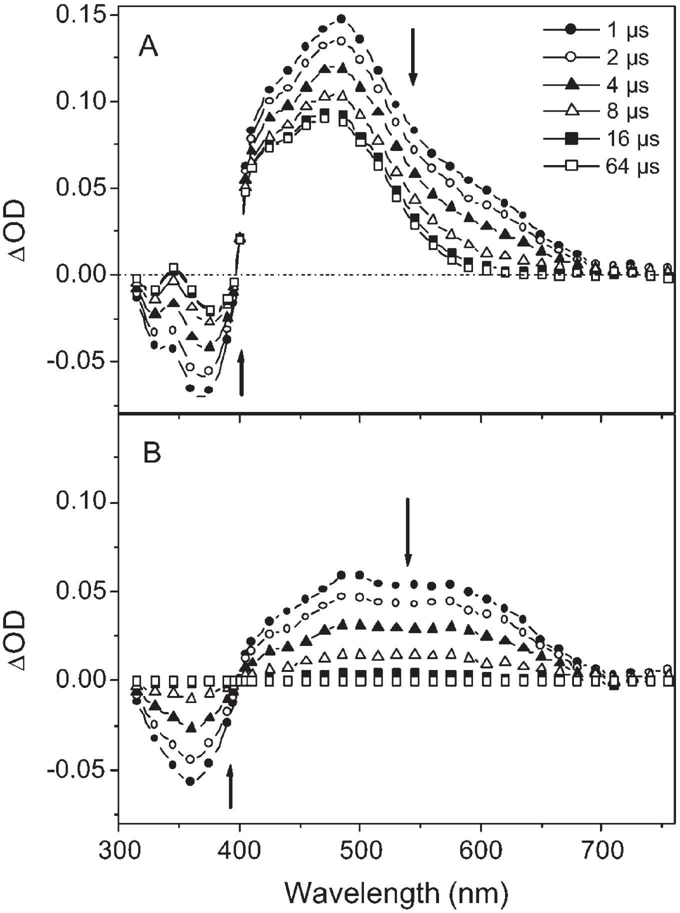


FIGURE 2 Transient absorption spectra of 8BT-C (2.5×10^{-4} M) in acetonitrile at different time delays after a 10 ns pulse excitation at 355 nm; (A) raw spectra; (B) spectra processed by subtracting the 64 ps spectrum at all times.

disappearance of the 550–650 nm shoulder and the partial decay of the bleaching signal with similar kinetics ($t_{1/2} \sim 5\,\mu s$). These kinetics appear strongly accelerated in the presence of oxygen in the solution, suggesting that they characterize the decay of the excited triplet state T_1 and the ground state repopulation. In contrast, the 485 nm absorption keeps a constant intensity over this time scale and is not sensitive to O_2. This band is unambiguously characteristic of the open form spectrum [3].

Taking off the contribution of this open form by subtracting the 64 μs spectrum from all spectra in Figure 2A, leads to the series of processed spectra shown in part B of Figure 2. This spectral evolution can be assumed to be exclusively characteristic of the $T_1 \rightarrow S_0$ relaxation process. To corroborate this assignment, the T_1 state of 8BT-C has been produced indirectly by triplet–triplet energy transfer using benzophenone as photosensitizer. Figure 3 shows transient absorption spectra obtained in the 0.5–8.0 μs time domain following 355 nm excitation of a mixture of benzophenone (3×10^{-3} M) and 8BT-C (1×10^{-3} M) in acetonitrile. For clarity, the triplet state absorption contribution of benzophenone has been subtracted in all spectra. These spectra show clearly the same absorption and bleaching bands as those in Figure 2B. The slow increase of these two signals matches the decay of the benzophenone triplet absorption, which indicates that photosensitization of 8BT-C actually takes place. Therefore, the 400–650 nm broad absorption band observed in the spectra of Figures 2B and 3, and thus the 550–650 nm shoulder in the 1000 ps spectrum of Figure 1 or in the 1 μs spectrum of Figure 2A, are unambiguously characteristic of the T_1 state absorption of 8BT-C.

The above results demonstrate that the cleavage of the spiro-carbon – oxygen single bond yielding the merocyanine form (photochromic route) occurs in the excited S_1 state in competition with the fluorescence

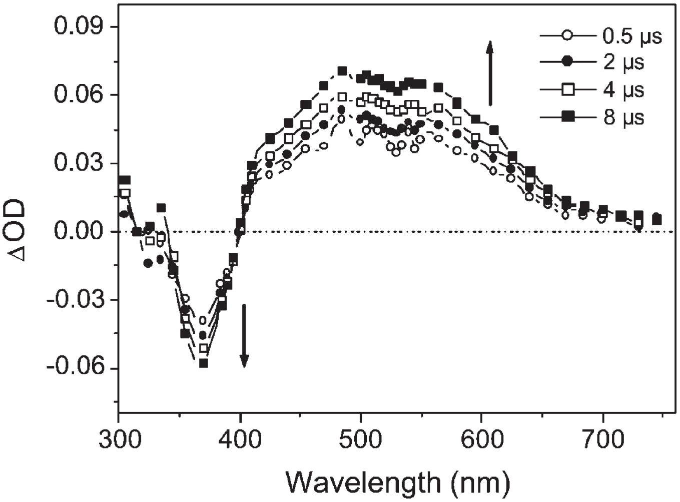
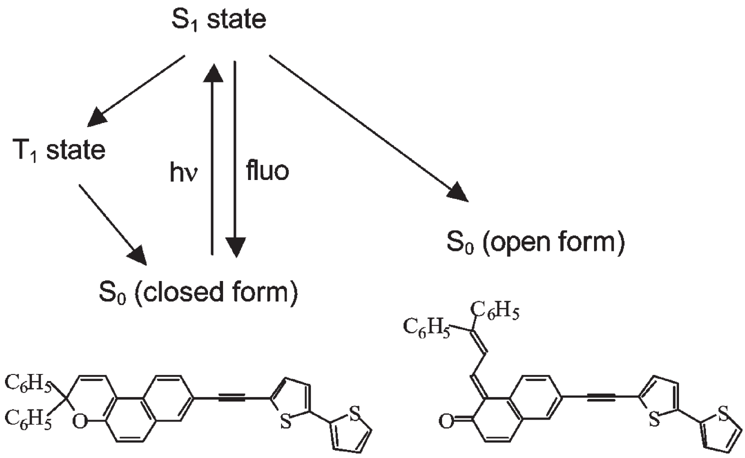


FIGURE 3 Transient absorption spectra recorded at different time delays after a 10 ns pulse excitation at 355 nm of a solution of 8BT-C (1×10^{-3} M) and benzophenone (3×10^{-3} M) in acetonitrile.



SCHEME 1 Schematic representation of the relaxation processes of 8BT-C after excitation.

($S_1 \rightarrow S_0$) and intersystem crossing ($S_1 \rightarrow T_1$) deactivation routes. The triplet state is not involved in the photochromism. This conclusion is consistent with a previous observation that, in thiophene linked *[2H]*-chromenes, the fluorescence intensity of the closed form varies inversely to the photochromism intensity [3]. The photophysics of 8BT-C is summarized in Scheme 1.

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