

Transient absorption investigation of the photophysical properties of new photochromic 3H-naphtho[2,1-b]pyran

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ABSTRACT: The photophysical and photochemical properties of two 3,3-diphenyl-3H-naphtho[2,1-b]pyrans substituted in position 8 by phenylethynyl and *p*-nitrophenylethynyl groups, respectively, 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 S₁ state. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: [2H]-chromene; 3H-naphtho[2,1-b]pyran; photochromism; photophysical properties; transient absorption

INTRODUCTION

Elaborating organic photofunctional molecules with potential applications for optoelectronic devices is an ambitious and challenging field of modern organic chemistry. One target among others is the conception of organic photoconductors and photo-switched conductors. In this regard, an interesting approach is, to incorporate a photochromic molecular system within a conducting polymer chain. One can expect that the electronic conjugation between two polymer half-chains attached to a photochromic molecule at strategic positions can be simply activated or deactivated by light irradiation via the photochromic transformation. This idea has recently motivated the synthesis of a series of model compounds elaborated by appending oligothiophenic chains to various photochromic 3H-naphtho[2,1-b]pyran molecules derived from the [2H]-chromene family (Chart 1).^{1–12} In this family, photochromism proceeds via the cleavage of the geminal diaryl carbon–oxygen single bond (C₃—O) of the chromene moiety.¹³ The reaction leads to a colored merocyanine form (open form, OF)

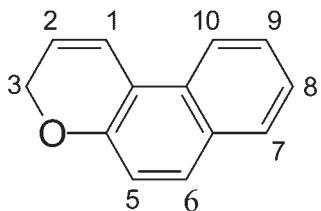
with extended π-conjugation that might couple electronically substituents in position 3 and 8 that are uncoupled in the closed form (CF). A molecular photo-switch behavior has been actually demonstrated for a 3H-naphtho[2,1-*b*]pyran compound substituted by bithiophenic groups in position 3 and 8.^{7,8} However, it has also been observed that the efficiency of photocolorability of the molecule decreases markedly or even vanishes when the substituted oligothiophenic chains become too long. For example, in a series of 3,3-diphenyl-3H-naphtho[2,1-*b*]pyrans substituted in position 8 by thiophene oligomers via an acetylenic junction, the photocolorability increases progressively as the number *n* of oligomeric thiophenic substituents increases from 0 to 2, but for *n* = 3 the compound does not show any photochromism.^{5,10} A similar effect was reported for naphthopyrans bearing oligothiophene substituents directly attached in position 3 or 8.¹⁴ A thorough investigation of the photophysical and photochemical properties of this family of compounds is required to understand the influence of the nature and electronic configuration of aromatic substituents on the energy relaxation pathways and photochromism efficiency. In recent spectroscopic studies of naphthopyrans^{14–20} and spironaphthoxazines,^{21–23} transient absorption was proved to be a very powerful technique to provide detailed information relative to the ring-opening mechanism and efficiency.

We present here a comparative analysis by transient absorption spectroscopy in the femtosecond to

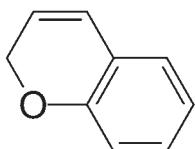
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3H-naphtho[2,1-b]pyran



[2H]-chromene

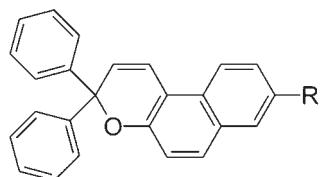
Chart 1.

microsecond time domain of two 3,3-diphenyl-3H-naphtho[2,1-*b*]pyran compounds substituted in position 8 by phenylethynyl and *p*-nitrophenylethynyl groups (Chart 2, **2** and **3**, respectively). The results are discussed in particular by analogy with those recently reported for the unsubstituted parent molecule (**1** in Chart 2)^{15,19} and for the compound substituted in position 8 by a dithienylethynyl group (**4** in Chart 2).²⁰

EXPERIMENTAL

Synthesis of 3,3-diphenyl-3H-naphtho[2,1-*b*]pyran substituted in position 8 by phenyl (**2**) and *p*-nitrophenyl (**3**) groups via an acetylenic junction were performed according to a procedure reported previously.^{3,10} Purification by column chromatography yielded the pure compound after recrystallization. **2**: m.p. 194–195°C, C₃₃H₂₂O (Found: C, 91.31; H, 4.98. Required: C, 91.21; H, 5.10). **3**: m.p. 208–209°C, C₃₃H₂₁O₃N (Found: C, 82.73; H, 4.32; N, 3.02. Required: C, 82.65; H, 4.41; N, 2.92). Acetonitrile and cyclohexane (Aldrich, spectrophotometric grade) were used as received.

The femtosecond transient absorption setup has been already described.²⁴ Briefly, it involves a 1 kHz Ti-sapphire laser system based upon a Coherent (MIRA



1	R = H
2	R = C≡C—C ₆ H ₅
3	R = C≡C—C ₆ H ₄ —NO ₂
4	R = C≡C—C ₄ H ₂ S—C ₄ H ₃ S

Chart 2.

900D) oscillator and a BM Industries (ALPHA 1000) regenerative amplifier. Pump excitations at 383 and 266 nm were obtained by frequency doubling the Ti-sapphire fundamental tuned at 766 nm or frequency tripling the fundamental tuned at 800 nm, respectively (0.3 mm BBO crystals). The pump pulse (~150 fs) power was limited to 1–3 μJ per pulse (0.1–0.3 mJ/cm²). A white light continuum probe pulse was generated at 766 or 800 nm in a CaF₂ plate. The pump-probe polarization configuration was set at the magic angle. The probe pulse was delayed in time relative to the pump pulse using an optical delay line (Microcontrol Model MT160–250PP driven by an ITL09 controller, precision ±1 μm). The overall time resolution (fwhm of the pump-probe intensity cross-correlation) was estimated to be about 300 fs from the two-photon (pump + probe) absorption signal in pure hexane. The time dispersion of the continuum light over the 300–700 nm region of analysis was about 0.8 ps. The transmitted light was analyzed by a CCD optical multichannel analyzer (Princeton Instrument LN/CCD-1340/400-EB detector + ST-138 controller). Sample solutions (2.5 × 10^{−4} M) were circulating in a flow cell with 2 mm optical path length. Data were accumulated over 3 min (~180000 pump-probe sequences).

The nanosecond transient absorption spectra were recorded in the 280–800 nm region using the 355 nm output of a Yag laser (7 ns, 1 mJ, 20 Hz) as pump excitation and a Xe flash lamp as the probe. Samples were contained in a quartz cell (1 × 1 cm² section) at a concentration adjusted to get an OD value of ~1.0 at 355 nm. Solutions were deaerated by bubbling N₂.

RESULTS AND DISCUSSION

3,3-diphenyl-8-(phenylethynyl)-3H-naphtho[2,1-*b*]pyran (**2**)

The absorption spectrum of **2** in cyclohexane (Fig. 1), similar to that obtained in acetonitrile, shows some resemblance with that reported for the parent 3,3-diphenyl-3H-naphtho[2,1-*b*]pyran molecule, **1**,¹⁹ with three groups of bands in the 200–400 nm region: an intense absorption peaking below 200 nm; a second strong band with vibronic maxima at 272, 285, and 302 nm, which corresponds probably to a of **1** transition showing vibronic components at 281, 300, and 313 nm; finally, a group of four much weaker components at 326, 339, 356, and 373 nm that may correlate with a transition of lowest energy (λ_{max} at 330, 345, and 360 nm) observed in the spectrum of **1**. No significant fluorescence emission could be detected in any solvent.

Figure 2 shows transient absorption spectra recorded in the 300–700 nm region at different time delays from 0.6 to 50 ps following 266 nm excitation of **2** (2.5 × 10^{−4} M) in cyclohexane. A restricted region (425–625 nm) of

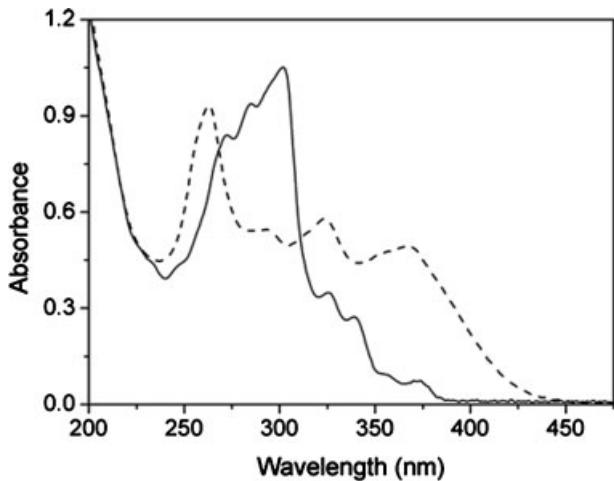


Figure 1. Absorption spectra of **2** (full line) and **3** (dashed line) in cyclohexane

comparable spectra obtained in the 0.4–20 ps time domain after 383 nm excitation is presented in the inset. Similar spectra were obtained in acetonitrile. The time evolution measured at all wavelengths upon 383 nm excitation can be fit with the same set of three exponential kinetics. The shortest time spectrum (0.4–0.6 ps), characterized by a strong band peaking in the 350–380 nm domain and a weaker one around 530 nm (more apparent upon 383 nm excitation), decays with a time constant of

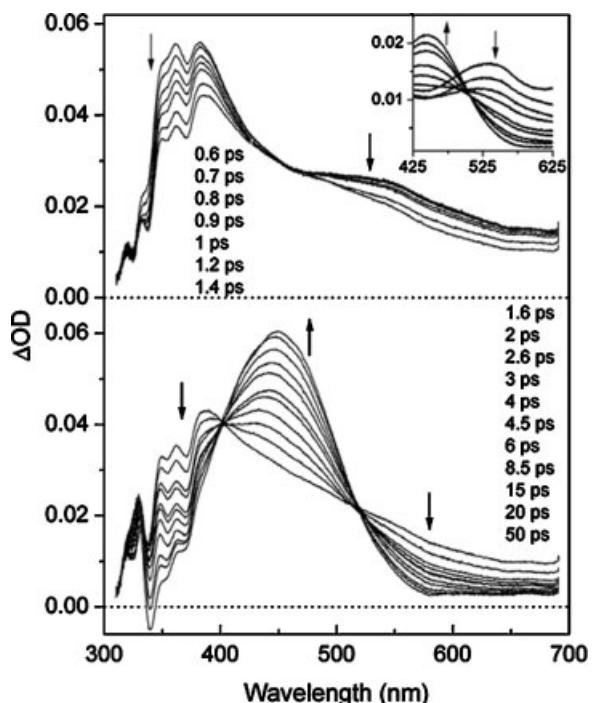
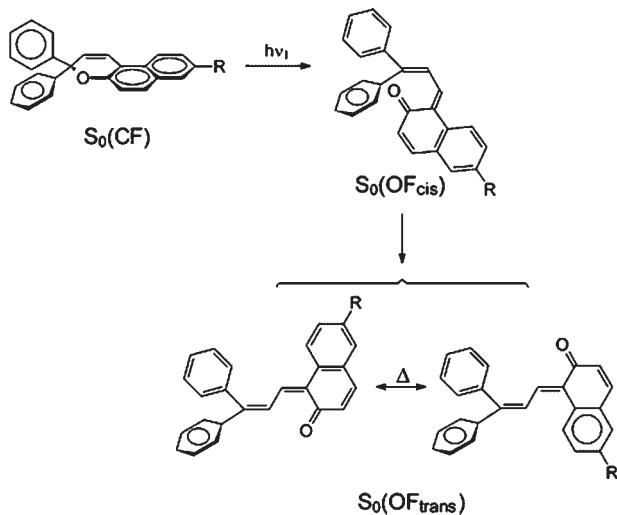


Figure 2. Transient absorption spectra (300–700 nm) of **2** (2.5×10^{-4} M) in cyclohexane at different time delays from 0.6 to 1.4 ps (top) and 1.6 to 50 ps (bottom) after 0.15 ps pulse excitation at 266 nm. Inset: enlargement of the 425–625 nm region of transient spectra recorded from 0.4 to 20 ps after 383 nm excitation. Vertical arrows indicate the signal evolution

0.28 ± 0.06 ps and yields a broad and diffuse spectrum maximizing around 390 nm and extending up to 700 nm. Then, this spectrum disappears whereas a third one described by a well-defined band at 450 nm rises concomitantly with isosbestic points at 402 and 520 nm. This evolution is characterized by a two-exponential kinetics of time constants $\tau_1 = 2.0 \pm 0.5$ and $\tau_2 = 10 \pm 2$ ps. No further spectral evolution is observed in the 50–1500 ps time domain. It can be seen in Fig. 2 that, at all times, the transient absorption signal in the 300–400 nm region is marked by the presence of a superimposed well-resolved negative band structure leading to absorption minima at 324, 339, 355, and 370 nm. These values match nicely the four lowest energy components of the steady-state absorption spectrum of **2** and thus can be readily ascribed to the ground state bleaching of the closed form (CF).

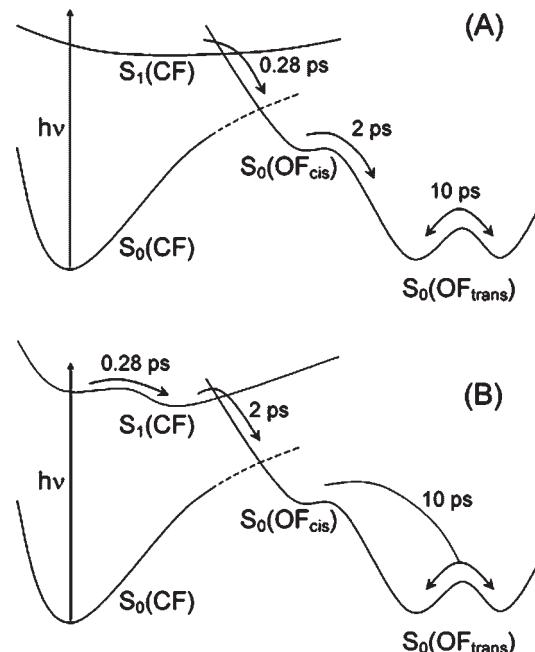
The overall spectral evolution observed for **2** in the picosecond region is somewhat comparable to that previously reported for the parent molecule **1**.^{15,19} We propose to ascribe the shortest time spectrum (530 nm band) to the lowest excited singlet state of CF, $S_1(\text{CF})$. The fact that this spectrum is more distinctly visible on 383 nm excitation than at 266 nm is probably due to the existence of additional relaxation processes in the latter case. In fact, it can be inferred from the absorption spectrum of **2** (Fig. 1) that direct population of $S_1(\text{CF})$ occurs at 383 nm whereas, at 266 nm, an upper excited state $S_n(\text{CF})$ is formed first, which then relaxes to $S_1(\text{CF})$ with a noticeable amount of excess energy. Since $S_1(\text{CF})$ is very short-lived (0.28 ps), its dynamics is thus expected to be intricately mixed up with the $S_n(\text{CF})$ relaxation and cooling dynamics. The visible S_1 absorption (λ_{max} at 530 nm) is located at intermediate position between the bands assigned previously to the S_1 state in **1** (500 nm)¹⁵ and in the 8-(dithienylethynyl) compound **4** (588 nm).²⁰ In the case of **4**, the S_1 state having a much longer lifetime (150 ps in acetonitrile), its assignment could be definitely confirmed by the observation of a signal of stimulated emission having same decay kinetics. For **1**, as for **2**, the shortest time spectrum observed in the spectrokinetic evolution was not as clearly apparent. It has been assigned to $S_1(\text{CF})$ ¹⁵ or to a primary photoproduct.¹⁹ Its decay time constant (0.45 ps,¹⁵ 0.43 ps¹⁹) is comparable to the 0.28 ps value ascribed here to the S_1 state lifetime of **2**.

The absorption band at 450 nm that grows beyond 1.4 ps with a two-exponential kinetics is typical of the trans merocyanine form, or open form, $S_0(\text{OF})$. By analogy with the mechanism suggested for **1**, we propose to ascribe the two growing times to the appearance of a first trans OF species and to its further evolution toward a thermal equilibrium between two trans isomers^{15,25} (Scheme 1). Obviously, the growth of OF is not concomitant with the $S_1(\text{CF})$ decay but starts only after its decay. This implies the existence of an intermediate species that is characterized by the broad and diffuse spectrum observed at 1.4 ps after decay of the $S_1(\text{CF})$



Scheme 1. Geometrical representation of the ground state closed form (CF) and cis/trans open forms (OF) of the 3,3-diphenyl-3H-naphtho[2,1-b]pyran compounds

spectrum. Recent CASSCF calculations of the excited-state ring-opening reaction coordinate in 2H-chromene (Chart 1) did not predict the existence of several well-distinguishable minima on the excited state surface. Instead they suggest that a rather flat region with very shallow and indefinite minimum extends without any significant barrier from the initial Franck-Condon excitation region to a transition state that leads directly to a conical intersection with the ground state surface.^{26,27} The transition state itself is almost barrierless. If a similar reaction pathway is assumed for **2**, the initial $S_1(\text{CF})$ species identified experimentally (0.4 ps spectrum) corresponds probably to the above shallow excited state minimum and it seems improbable that the following transient species (1.4 ps spectrum) also belongs to the excited state surface. It can rather be ascribed to a metastable ground state cisoid OF isomer, which is necessarily the first product of the ring-opening reaction (see Scheme 1). In this hypothesis, the 0.28 ps time constant corresponds to the ring-opening process, the 2.0 ps kinetics to a ground state cis-trans isomerization of the OF species, and the 10 ps kinetics to the thermal equilibrium between the two trans forms, as represented in Scheme 2A. However we cannot rule out the eventuality of a reaction pathway for **2** more complex than that calculated for [2H]-chromene with, for instance, a weak excited state barrier between an excited state minimum close to the Franck-Condon region and a second shallow minimum farther on the excited surface, before the transition state. In this case the 0.28 ps time constant would be due to a restricted excited-state structural relaxation, the 2.0 ps kinetics to the ring-opening process, and the 10 ps one to the overall ground state evolution (cis-trans isomerization and thermal equilibrium between the trans forms), as it is displayed in Scheme 2B. Although this hypothesis seems



Scheme 2. Schematic representation of two possible reaction pathways for the ring opening process characterized by the absence (A) or existence (B) of a weak excited-state barrier

more consistent with the fact that the spectra of the first two transient species (0.4 and 1.4 ps, respectively) are broad and cover the whole visible range, it cannot be ascertained definitely.

Figure 3, part A, presents transient absorption spectra of a deaerated solution of **2** in cyclohexane recorded from 0.5 to 32 μ s after excitation by 7 ns laser pulses at 355 nm. In the 300–550 nm range, these spectra are comparable to the 50 ps spectrum just discussed, with the bleach signal around 350 nm and the absorption band of the OF species at 450 nm. These features keep nearly constant intensity on the 0.5–32 μ s time period apart from a weak increase in absorption on the blue side of the OF band. In addition, one observes a weaker band at 630 nm that decays within 20 μ s. Subtracting the final spectrum (100 μ s) to all spectra leads to the spectral evolution displayed in Fig. 3, (part B), characterized by a negative band in the 350–450 nm region and the 630 nm absorption band. Both signals decay with the same time constant of 6.7 μ s, indicating that they characterize the same event. This decay is strongly shortened in the presence of oxygen, which suggests a triplet state assignment for the 630 nm absorption band. The negative band corresponds to the position of the OF absorption that is too much subtracted upon removing the 100 μ s spectrum. It reveals that the triplet state species relaxes by intersystem crossing (ISC) to the OF ground state. As a confirmation, the constant intensity of the \sim 350 nm bleach signal in Fig. 3 (part A) indicates that there is no repopulation of $S_0(\text{CF})$ during the triplet state decay. An interrogation concerns the identity of the triplet state species. It might be the triplet state of the CF molecule, $T_1(\text{CF})$, formed from $S_1(\text{CF})$ in

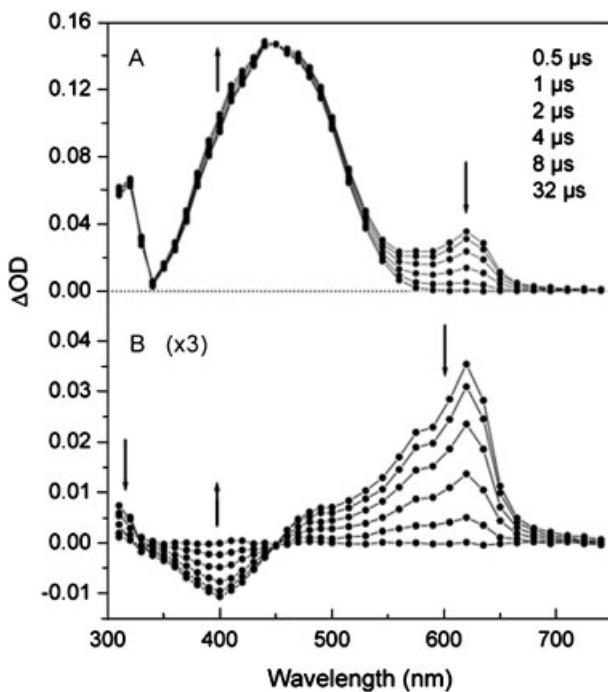


Figure 3. Transient absorption spectra recorded at different time delays after a 7 ns pulse excitation at 355 nm of a N_2 -purged solution of **2** ($\text{OD} = 1$ at 355 nm) in cyclohexane. (A) raw spectra; (B) spectra processed by subtracting the 100 μs spectrum at all times. Vertical arrows indicate the signal evolution

parallel to the ring-opening reaction and leading itself to $S_0(\text{OF})$ via ring-opening. Such a reaction scheme implies that both the S_1 and T_1 states of CF do contribute to the photochromism of **2**. However, in this hypothesis, the T_1 state should appear concomitantly with the decay of the S_1 state, that is, within 1 ps. This is in contradiction with the fact that the T_1 state band at 630 nm is not observed in the picosecond time domain (Fig. 2). A more convincing interpretation is to ascribe the 630 nm absorption to the OF triplet state, $T_1(\text{OF})$, produced by reexcitation, by a late photon of the nanosecond pump pulse, of the $S_0(\text{OF})$ species previously formed from excitation of the initial CF molecule by an early photon of the same pump pulse. Such a sequential two-step process is possible in the nanosecond excitation regime since the pulse duration is much longer than the time of formation of $S_0(\text{OF})$ via ring-opening. On the contrary, it cannot happen in the femtosecond regime since the excitation pulse is clearly shorter than the $S_0(\text{OF})$ appearance time. Accordingly, the negative band in Fig. 3 (part B) is a bleach signal due to the depletion of photoproduced merocyanine population by late photons of the nanosecond pump pulse.

3,3-diphenyl-8-(*p*-nitrophenylethynyl)-3H-naphtho[2,1-*b*]pyran (3)

The absorption spectrum of **3** in cyclohexane (Fig. 1, dashed line), similar to that obtained in acetonitrile, is

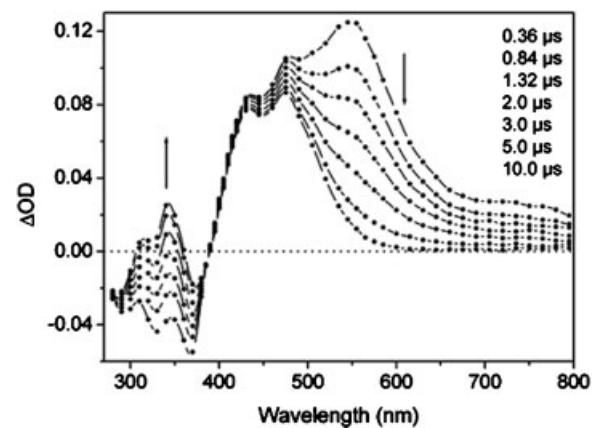


Figure 4. Transient absorption spectra recorded at different time delays after a 7 ns pulse excitation at 355 nm of a N_2 -purged solution of **3** ($\text{OD} = 1$ at 355 nm) in acetonitrile. Vertical arrows indicate the signal evolution

quite different from that recorded for the **1**¹⁹ and **2** molecules, with much stronger absorption strength in the blue region up to 450 nm (λ_{max} at 262, 293, 323, and 368 nm).

Spectra obtained in the 0.36–10 μs time domain for a deaerated solution of **3** in acetonitrile are shown in Fig. 4. A negative band in the 300–400 nm region, with minima at 290, 329, and 368 nm, is likely due to the CF ground state bleach as it matches the lowest energy components of the absorption spectrum (Fig. 1). Its intensity decreases partially within 10 μs and then remains nearly constant at longer time. A positive band at 548 nm decays entirely with the same kinetics as the transient part of the CF bleach (time constant $2.1 \pm 0.1 \mu\text{s}$). Both this absorption and the bleach kinetics appear significantly shortened in aerated solutions. We thus ascribe the 548 nm band to the CF excited triplet state, $T_1(\text{CF})$, which decays by ISC to the ground state $S_0(\text{CF})$. A second absorption signal centered around 450 nm and superimposed on the blue side of this T_1 absorption, with two peaks at 431 and 474 nm, keeps a constant intensity on the whole microsecond time range. Its intensity, as well as the intensity of the residual CF bleach observed after decay of T_1 , is not sensitive to the presence of oxygen. The position of this absorption is typical of the open form (merocyanine) species, $S_0(\text{OF})$. Its kinetic stability during the decay of $T_1(\text{CF})$ indicates that the ring-opening process occurs exclusively from the S_1 state, that is, the T_1 state of CF does not contribute to the photochromism of **3**. ISC is thus a deactivation route of $S_1(\text{CF})$ competing with the photochromic reaction.

Let's consider now the spectral evolution in the picosecond time domain. Figure 5 shows transient absorption spectra recorded in the 390–770 nm region at different time delays from 2 to 50 ps following 383 nm excitation of **3** ($2.5 \times 10^{-4} \text{ M}$) in acetonitrile. An initial broad band extending as far as 650 nm and showing a sharp maximum at 425 nm, truncated on its high

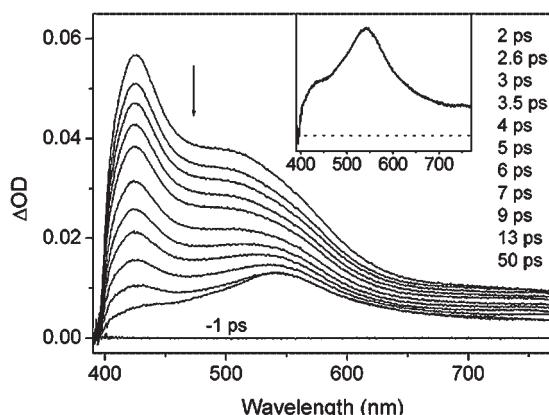
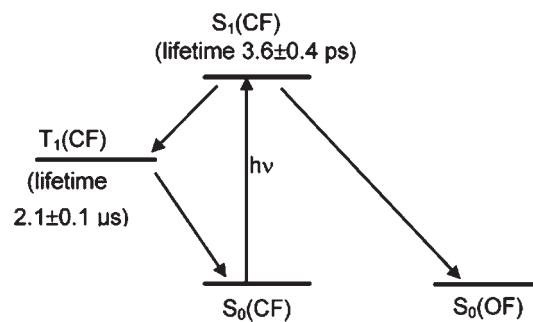


Figure 5. Transient absorption spectra (390–770 nm) of **3** (2.5×10^{-4} M) in acetonitrile at different time delays from 2 to 50 ps after 0.15 ps pulse excitation at 383 nm. Inset: enlargement of the 50 ps spectrum. The vertical arrow indicates the signal evolution

frequency side by the 400 nm filter used to stop the pump excitation light, and a shoulder around 500 nm, decays with a time constant of 3.6 ± 0.4 ps. After complete decay, a residual spectrum is observed at 50 ps (inset of Fig. 5), characterized by a band peaking at 542 nm and a shoulder around 445 nm. No further spectral evolution is perceptible from 20 to 1500 ps. The 50 ps spectrum matching approximately that observed at 0.36 μ s (Fig. 4), the 542 nm band and 445 nm shoulder seen at 50 ps can be readily ascribed, by analogy, to the T_1 state of CF and ground state of OF, respectively, produced concurrently from $S_1(\text{CF})$. The somewhat weaker intensity of the $T_1(\text{CF})$ band relative to the $S_0(\text{OF})$ band in the 0.36 μ s spectrum compared to the 50 ps spectrum is consistent with the fact that partial decay of $T_1(\text{CF})$ is expected on this time interval whereas $S_0(\text{OF})$ is stable. It can also result from some variation of the relative efficiency of the ISC and ring-opening processes on changing the pump excitation from 355 nm (nano-microsecond experiment) to 383 nm (femto-picosecond experiment). The initial broad spectrum observed at 2 ps in Fig. 5 is likely due to the $S_1(\text{CF})$ state, precursor of $T_1(\text{CF})$ and $S_0(\text{OF})$. This spectrum shows manifest analogies with that ascribed above to the CF S_1 state of **2** (band maximum in the blue region, broad shoulder at 500–550 nm) but the S_1 lifetime is much longer in the case of **3**. This longer S_1 lifetime reveals a higher excited state barrier toward the ring opening coordinate, which is consistent with the fact that $T_1(\text{CF})$ is produced concurrently with the OF species. It can also explain the observation that the yield of the OF species, as roughly estimated from the intensity of the ~ 450 nm absorption band at 50 ps relative to the intensity of the initial $S_1(\text{CF})$ absorption, appears much lower in **3** than in **2**. The overall photoinduced processes for **3** in acetonitrile are summarized in Scheme 3.

In cyclohexane, the spectra recorded in the 0.5–64 μ s domain (Fig. 6, part A) show, as in acetonitrile, a negative bleach band below 400 nm due to the CF ground state



Scheme 3. Schematic representation of the relaxation processes after UV excitation of **3** in acetonitrile

depletion, a transient absorption band at 540 nm corresponding to the $T_1(\text{CF})$ state and a long-lived absorption band at 450 nm corresponding to $S_0(\text{OF})$. An additional transient absorption band is observed at 631 nm, which is, as the 630 nm band found in the case of **2**, absent in the spectra recorded upon excitation with femtosecond laser pulses. In deaerated solutions, the 540 and 631 nm bands decay with two different single exponential kinetics with time constants of 2.7 ± 0.1 and 5.0 ± 0.1 μ s, respectively. The kinetics are both significantly shortened in the presence of oxygen. These absorption bands can thus be ascribed to two distinct excited triplet states. One notes moreover in Fig. 6 (part A) a weak increase in absorption on the blue side of the merocyanine band, around 420 nm, from 0.5 to 64 μ s. At 30 μ s, after complete decay of the 540 and 631 nm bands, only the $S_0(\text{OF})$ absorption at 450 nm and the corresponding CF bleach below 400 nm remain present and no

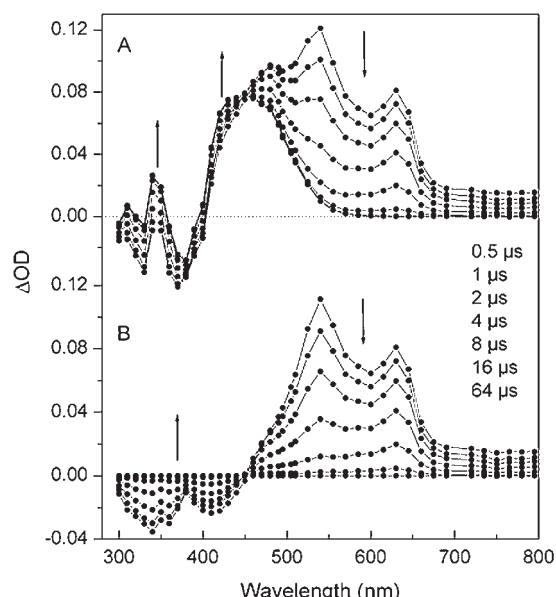
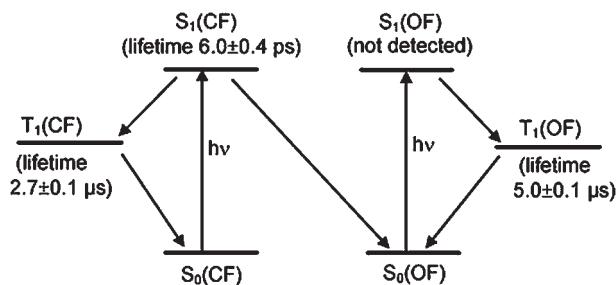


Figure 6. Transient absorption spectra recorded at different time delays after a 7 ns pulse excitation at 355 nm of a N_2 -purged solution of **3** ($\text{OD} = 1$ at 355 nm) in cyclohexane. (A) raw spectra; (B) spectra processed by subtracting the 64 μ s spectrum at all times. Vertical arrows indicate the signal evolution



Scheme 4. Schematic representation of the relaxation processes after UV excitation of **3** in cyclohexane

further spectral evolution is detected in the microsecond time domain. Subtracting the final spectrum (64 μ s) to all spectra leads to the spectral evolution shown in Fig. 6, part B. It is characterized by the decay of the 540 and 631 nm positive bands and of two negative signals in the 300–380 and 380–450 nm ranges. As discussed above, the former characterizes the CF bleach and decays with the same kinetics as the CF triplet band at 540 nm. This kinetics (2.7 μ s) corresponds thus to the ground state repopulation of the CF species from its T_1 state, as in acetonitrile. The negative band in the 380–450 nm range is lying at the position of the S_0 (OF) absorption and decays with the same kinetics as the triplet band at 631 nm. According to these observations, we ascribe the 631 nm absorption to the triplet state of the OF species, T_1 (OF), produced exclusively upon nanosecond excitation, as in the case of **2**, by a sequential two-step process: the S_0 (OF) species just produced on excitation of the CF molecule is immediately reexcited to the triplet state T_1 (OF) by the same laser pulse, causing a S_0 (OF) bleach. This bleach signal is clearly evidenced by the negative band in the 380–450 nm range in Fig. 6, part B. Repopulation of S_0 (OF) from the decay of T_1 (OF) (5 μ s kinetics) manifests itself by the annihilation of this bleach signal. It also corresponds to the increase in absorption observed around 420 nm in Fig. 6, part A. Scheme 4 summarizes the whole reaction pathway in cyclohexane. It is clear on this scheme that reexcitation of the OF species has no chance to occur in the femtosecond measurements since the time of formation of this species (6 ps) is much longer than the laser pulse duration (150 fs).

The reason why the sequential two-step formation of the OF triplet state does not occur in acetonitrile is not clear. A possible explanation could be a solvent dependent ordering of the OF lowest excited singlet and/or triplet states with, for instance, an inversion of close-lying $n\pi^*$ and $\pi\pi^*$ states on going from polar to nonpolar solvents modifying strongly the yield of ISC.

CONCLUSIONS

The above results demonstrate that, in both the **2** and **3** compounds, the cleavage of the geminal diaryl carbon –

oxygen single bond yielding the merocyanine form (photochromic route) occurs in the excited S_1 state, as in the parent molecule **1**. In the nitro compound, the reaction is in strong competition with the intersystem crossing ($S_1 \rightarrow T_1$) deactivation route. However, the triplet state is not involved in the photochromism. The absorption maximum of the OF species is slightly red-shifted in going from **1** (420 nm^{15,19}) to **2** and **3** (450 nm), then to **4** (485 nm²⁰). This shift parallels an increase in size of the π skeleton of the chemical group substituted in position 8, which suggests that there is some π delocalization between this group and the naphthopyran chromophore in the OF structure. Finally, an additional O_2 sensitive transient absorption band, ascribed to the OF triplet state produced by sequential two-step process, is observed in cyclohexane solvent exclusively upon nanosecond excitation. This reaction has been accounted for by the fact that the lifetime of the OF form produced from excitation of the CF molecule by a nanosecond laser pulse is much shorter than the duration of this pulse, which allows the OF form to be also excited by late photons of the same laser pulse.

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