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Investigations by NMR spectroscopy of a polyphotochromic system involving two entities, spirooxazine and naphthopyran, linked by a *Z*-ethenic bridge

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Received (in Cambridge, UK) 8th July 2002, Accepted 25th September 2002
First published as an Advance Article on the web 29th October 2002

The biphotochromic molecule, made up of spirooxazine and naphthopyran entities linked by a *Z*-ethenic bridge, was synthesised to extend the conjugation and obtain photomerocyanines absorbing all the visible spectrum. Photochromic behaviour was studied by ^1H and ^{19}F NMR spectroscopy, using previous NMR results obtained for spirooxazine alone and naphthopyran alone. At first, studies performed at low temperature (228 K) showed a clean conversion between closed and open structures with the demonstration of mono- and bi-opening of the biphotochromic molecule and with a *Z*/*E* isomery of the ethenic bridge. In contrast, studies at ambient temperature indicated intramolecular cyclisation stabilising the photomerocyanines. An unexpected thermal opening of the naphthopyran entity in the cyclised form was also observed. A thermal cyclisation–oxidation reaction occurred, implying an irreversible loss of photochromic properties. By carrying out experiments on degassed samples, a **TC-TT** isomery of open naphthopyran was obtained, leading to a consistent equilibrium between the different stereoisomers of the photomerocyanines.

Introduction

Naphthopyrans[1,2] and spironaphthoxazines[3] are two photochromic families well-known for their favourable properties such as a high number of coloration–decoloration cycles and remarkable fatigue resistance. Association of both entities offers complementary colours (red and blue) upon irradiation, which is of great interest for industrial applications. The bis(4′-fluorophenyl)-3*H*-naphthopyran molecule leads to two photomerocyanine forms, **TC** and **TT** isomers, with very different kinetic rates of bleaching,[4] while the irradiation of spiro(indoline-naphthoxazine) produces two photomerocyanines (the most stable **TTC** and **CTC** isomers), with similar kinetic constants of bleaching.[5] For both families, characteristic ^1H and ^{19}F NMR resonances have proved the isomery of the different structures and concord with results obtained by spectrophotometric methods.[3,6] We have recently demonstrated that NMR spectroscopy is a powerful tool for studying the behaviour of biphotochromic structures (bi-spirooxazine[7] and bi-naphthopyran[8]). In the course of our investigations, we have obtained the following results on the kinetic and structural behaviour of a biphotochromic molecule, containing spirooxazine and fluoro-naphthopyran entities joined by a *Z*-ethenic bond. The investigations were performed by ^1H and ^{19}F NMR spectroscopy at low and ambient temperature making it possible to follow the kinetic behaviour of each photoproduct separately and to identify each of them. This molecule, which presents a particular coloration consistency, has also been investigated by Mazzucato and co-workers[9] by spectrophotometrical methods and by HPLC at ambient temperature, making it possible to determine its intrinsic properties (quantum yields, wavelengths and molar absorption coefficients of the maxima of the photoproducts). The identification of photoproducts was backed by information from a parallel NMR study, which is developed here.

Results

Behaviour at low temperature

After UV irradiation of **CC**-*Z* in acetone-d$_6$ at 228 K, ^1H and ^{19}F NMR spectra were recorded at regular time intervals.

The ^{19}F NMR spectra (Fig. 1) show several new resonances, split into two regions. That around −115 ppm indicates a closure of the naphthopyran entity with two different resonances for the fluorine atoms when the spirooxazine entity is closed and with a single resonance for both fluorines when the

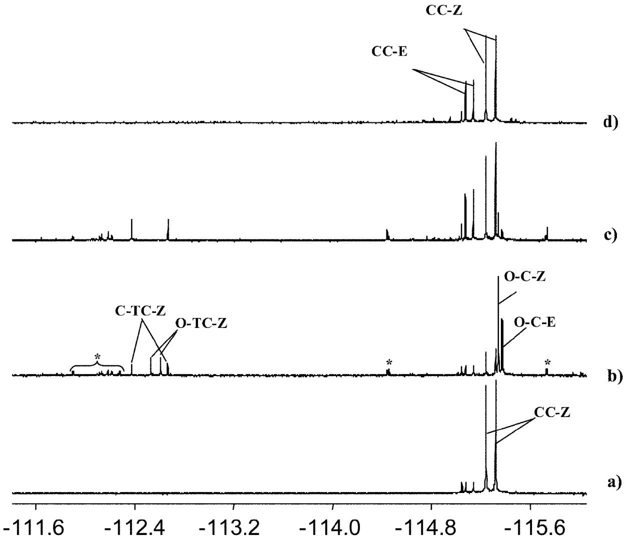


Fig. 1 ^{19}F spectra (a) before, (b) just after irradiation, (c) 4 h after irradiation, and (d) at the end of the bleaching of **CC**-*Z* at 228 K (*: weak unknown forms).

DOI: 10.1039/b206574f

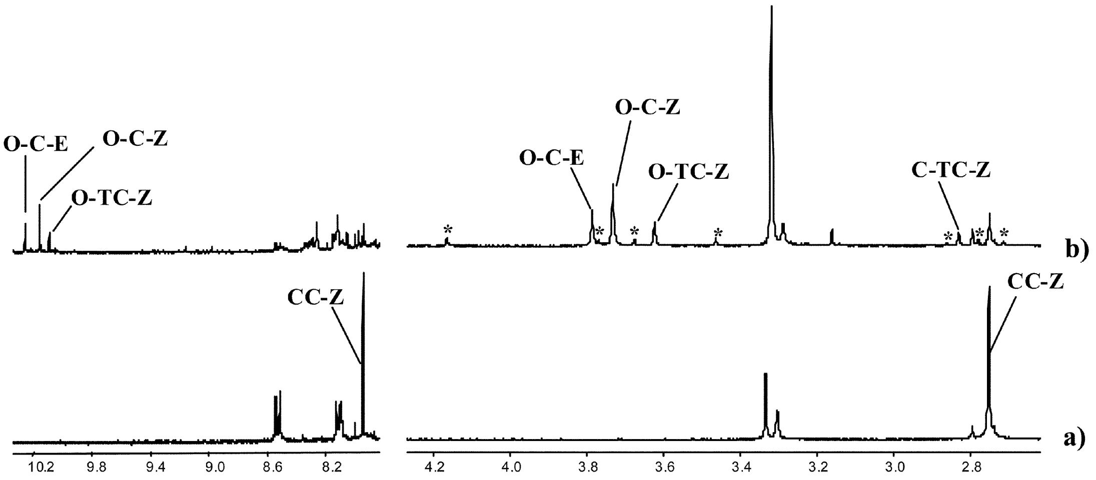


Fig. 2 ^1H spectra (a) before and (b) just after irradiation (*: weak unknown forms).

spirooxazine entity is open. The second, around −112 ppm is characteristic of an open naphthopyran with two peaks for the two fluorine atoms.[4] Consequently, the signals at −115.34 ppm for **O-C-*Z*** (**O** characterising **O**pen spirooxazine, **C** the **C**losed naphthopyran and *Z* the isomery of the bridge) and −115.37 ppm for **O-C-*E*** (**O**pen spirooxazine, **C**losed naphthopyran with *E* bridge) are assigned to two photoproducts with open spirooxazine (**TTC** isomer) and closed naphthopyran. In the same way, the resonances at −112.53 and −112.61 ppm, **O-TC-*Z*** (**O**pen spirooxazine, **TC**-open naphthopyran with *Z* bridge), and those at −112.38 and −112.67 ppm, **C-TC-*Z*** (**C**losed spirooxazine, **TC**-open naphthopyran with *Z* bridge), are attributed to structures having open naphthopyran.

At the same time, the ^1H NMR spectra (Fig. 2) indicate the presence of new structures. The opening of spirooxazine is characterised by some significantly different chemical shifts for N–CH_3 around 3.7 ppm and aromatic $H_{2'}$, around 10.1 ppm.[5] When this entity is in the closed configuration, these protons give signals at 2.75 and 7.94 ppm, respectively. Consequently, the NCH_3 signal at 2.83 ppm, **C-TC-*Z***, characterises a photoproduct with closed-spirooxazine while the three others at 3.62, 3.73, and 3.78 ppm confirm three structures with open spirooxazine, in correlation with the three $H_{2'}$ resonances around 10.1 ppm, **O-TC-*Z***, **O-C-*Z*** and **O-C-*E***, respectively.

Finally, the measurement of peak intensities allows for a correlation of the structures deduced from ^{19}F NMR with those from ^1H NMR. Four major concentration photoproducts are formed on UV irradiation, one corresponding to a bi-opening (**O-TC-*Z***) and the three others assigned to mono opening (**O-C-*Z*** and **O-C-*E*** with open spirooxazine, and **C-TC-*Z*** with open naphthopyran).

To attribute the exact isomery of the ethenic bridge to each separate entity in the different photoproducts, their evolution was followed by measuring ^{19}F and NCH_3 intensities.

Thermal evolution (Fig. 3) showed the recovery of the initial **CC-*Z*** structure, as well as an increase in a second one, identified as its geometric isomer **CC-*E*** ($^3J_{a-b} = 16.5$ Hz). These two closed structures result from the disappearance of four photoproducts, through a simple mechanism (Scheme 1).

The resolution of this system leads to the calculation of the kinetic rate constants of bleaching, listed in Table 1. The values concord with those previously reported for spirooxazine[5] and naphthopyran[4] at low temperature.

Behaviour at ambient temperature

The behaviour observed at low temperature is typical for the opening–closing of the biphotochromic system. Spectrophotometric studies at ambient temperature in toluene solution showed a different behaviour with coloration consistency.[9]

Table 1 Thermal constants of bleaching of **CC-*Z***

	Acetone	
Open forms	k_A/s^{-1}	
O-C-*Z*	k_4	1.0×10^{-4}
O-C-*E*	k_5	1.2×10^{-4}
O-TC-*Z*	k_1	1.3×10^{-4}
	k_3	5.2×10^{-5}
C-TC-*Z*	k_2	2.2×10^{-5}

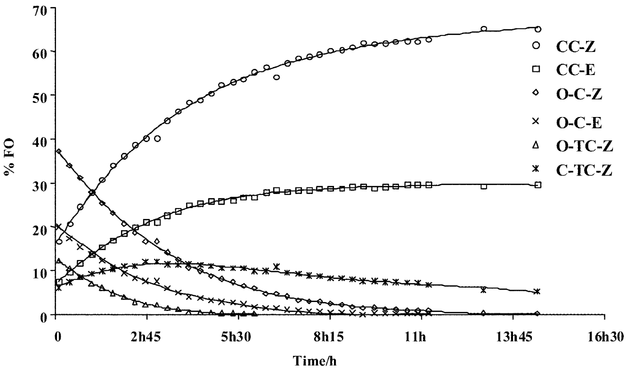


Fig. 3 Thermal evolution of **CC-*Z*** at $T = 228$ K in acetone.

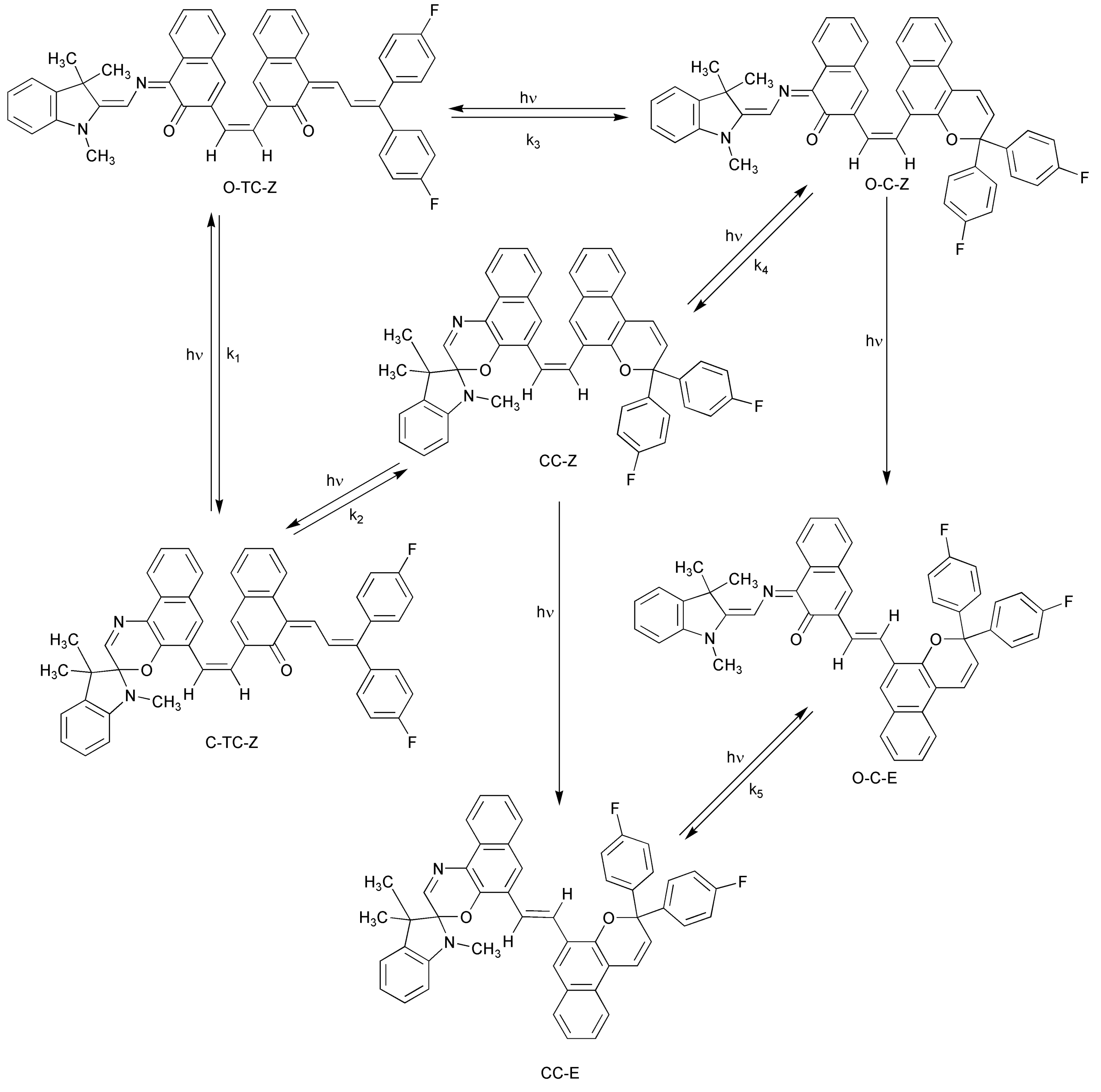
According to the same procedure as previously used, ^1H and ^{19}F NMR spectra were recorded at ambient temperature after irradiating **CC-*Z*** in toluene-d_8.

The ^{19}F NMR spectrum (Fig. 4b) confirms the formation of two photoproducts. Two signals with similar intensities at −112.76 and −113.80 ppm are attributed to a low-concentration structure (**O-C-DPh**), with the closed naphthopyran entity (chemical shifts close to those of **CC-*Z***). The two other signals at −111.59 and −111.83 ppm belong to a major concentration structure (**O-TC-DPh**), with the open naphthopyran. The isomery of the latter is deduced to be **TC** due to the deshielded chemical shift of H_2 at 8.78 ppm (Fig. 5).[4]

Typical signals at 2.94, 8.44, and 9.71 ppm (**O-C-DPh**) and at 2.95, 8.52 and 9.82 ppm (**O-TC-DPh**) correspond to NCH_3, $H_{10'}$ and $H_{2'}$ respectively. They characterise an opening of the spirooxazine entity in both photoproducts.

Finally, two doublet signals of high intensity are detected at 4.65 and 4.72 ppm and are directly assigned to H_6 and $H_{6'}$ protons.[7] They prove that an electrocyclisation occurred to produce a dihydrophenanthrenic structure, **O-TC-DPh**. The same conclusion based on the presence of two other doublet resonances of lower intensity at 4.43 and 4.57 ppm, can be deduced for the structure **O-C-DPh**.

These observations are summarized in Scheme 2.



Scheme 1

Thermal evolution shows firstly a disappearance of the mono-open structure, **O-C-DPh**, while the resonance of the second structure, **O-TC-DPh** increases (Fig. 4c). This phenomenon indicates a thermal opening of naphthopyran (k_{Δ} = 2 × 10^{-3} s^{-1}) at 293 K. Finally, an oxidative reaction takes place and leads to a phenanthrenic structure, resulting in the reclosing of both open entities. Muzskat[10] reported that the (*Z*)-stilbene-like molecule is known to show a photocyclisation, to produce dihydrophenanthrene, which irreversibly converts to phenanthrene, by hydrogen elimination with oxygen.[11] Two phenanthrenic-type molecules **CC-Ph$_1$** and **CC-Ph$_2$** are produced and are described as diastereoisomers, due to the asymmetrical carbon atom C_2 of the spirooxazine moiety and the helical-type shape of dibenzophenanthrene. The structure of these two diastereoismers have been proved through 2D NMR experiments.[7]

To suppress oxidation phenomena, studies have been carried out with degassed samples. The formation of the cyclised form (**O-TC-DPh**) after UV irradiation has been substantiated, but thermal evolution shows that another reaction rather than oxidation occurs. This new reaction does not lead to a reversion of the initial closed form, but produces a new structure (**O-TT-DPh**). In the ^{19}F NMR spectrum (Fig. 6), the signals at −110.92 and −111.64 ppm prove that the naphthopyran entity is always present in an open configuration. In the ^{1}H spectra (Fig. 7), the two doublet signals at 4.70 ppm and 4.72 ppm indicate a dihydrophenanthrenic structure and the characteristic signals at 2.94 ppm and 9.81 ppm for NCH_3 and $H_{2'}$, respectively, confirm the opening of the spirooxazine. The decrease in the doublet signal H_2 at 8.78 ppm for **O-TC-DPh** proves that the thermal evolution corresponds to a **TC-TT** isomery of the naphthopyran moiety. This reaction reaches equilibrium after one day (Fig. 8) with $k_1 = 4.5 \times 10^{-5}$ s^{-1} and $k_2 = 3.0 \times 10^{-5}$ s^{-1} (Scheme 2).

Conclusion

The investigation of **CC-*Z*** on UV irradiation at low temperature showed a significant conversion to expected photomerocyanines (mono- and bi-opening). The process is thermally reversible and no cyclised structure was produced. A bleaching mechanism was established, in which the disappearance of the bi-open structure (**O-TC-*Z***) occurred firstly by the closure of spirooxazine entity, followed by the closure of naphthopyran moiety.

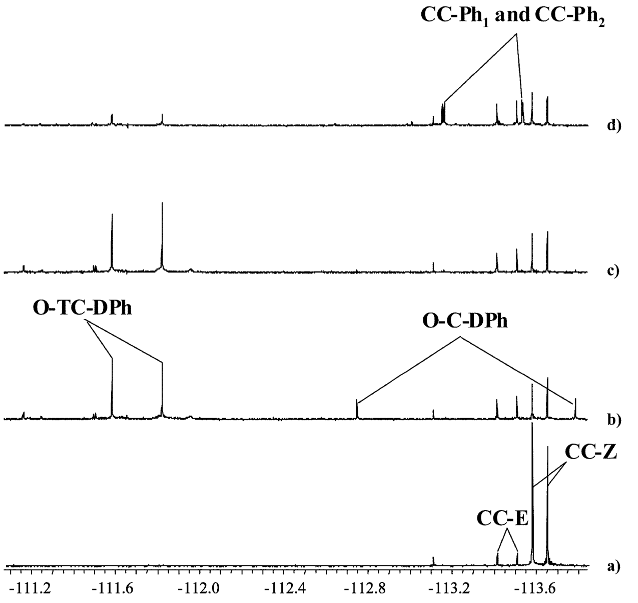


Fig. 4 ^{19}F spectra (a) before irradiation, (b) after irradiation, (c) after half an hour, and (d) after several days at ambient temperature.

The behaviour at ambient temperature is rather different, because of an intramolecular reaction, leading to a dihydrophenanthrenic-type structure (**O-C-DPh**), followed by an unprecedented thermal opening of the naphthopyran moiety (**O-TC-DPh**). An irreversible loss of photochromic properties is then consecutive to the formation of oxidised structures. The investigation performed on degassed samples showed an almost complete suppression of oxidation, but reformation of the initial **CC-*Z*** structure has not yet been observed. Instead of this expected reclosure, a **TC-TT** isomery occurred and led to a consistent equilibrium with high stability of the cyclised forms (**O-TC-DPh** and **O-TT-DPh**).

This work shows that high resolution ^{1}H and ^{19}F NMR spectroscopy is a promising tool to study polyphotochromic compounds: the number and the structure of each photomerocyanine can be unambiguously determined, as well as the structures of the oxidized photoproducts. In addition, the concentrations of the different structures can be directly measured from NMR spectra in given conditions. This offers a significant advantage towards the understanding of photochromic behaviour.

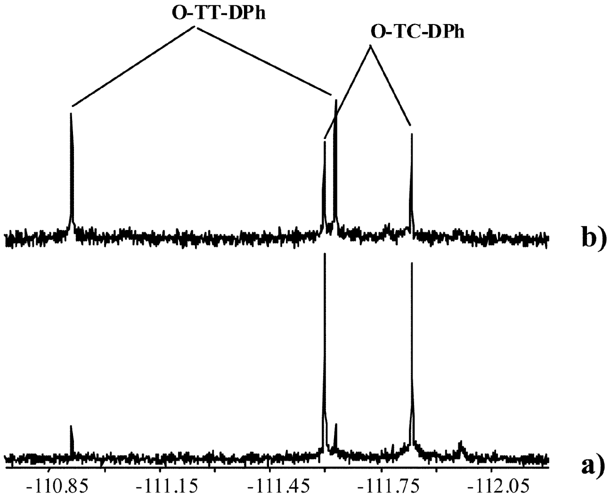


Fig. 6 ^{19}F NMR spectra of the degassed sample at ambient *T* after irradiation, (a) *t* = 30 min and (b) *t* = 12 h.

Experimental details

Materials

The bi-system investigated (Scheme 3) is the 5′[2-(3,3-bis-(4′-fluorophenyl)-[3*H*]naphto[2,1-*b*]pyran-5-yl)vinyl][1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphth[2,1-*b*] [1,4]oxazine] (**CC-*Z***, **C**losed spirooxazine-**C**losed naphthopyran with *Z*-ethenic bridge).[12]

Photostationary state experiments and NMR spectroscopy

The concentration of the sample is 5×10^{-3} M, in toluene-d$_8$ or in acetone-d$_6$. The sample was irradiated in the NMR tube (5 mm), in a home-built apparatus previously described,[13] equipped with a 1000 W Xe–Hg high-pressure lamp (Oriel), filtered by a band-pass glass filter (Lot–Oriel, 011FG09: $259 < \lambda < 388$ nm with $\lambda_{max} = 330$ nm). Irradiation and NMR experiments were performed at 228 and 293 K. After 10 min irradiation, the NMR sample tube was rapidly transferred to the thermo-regulated probe.

The ^{1}H and ^{19}F NMR spectra were carried out on a Bruker AC300P NMR or DPX-300 spectrometers equipped with a QNP probe. Tetramethylsilane (TMS) was used as an internal standard for ^{1}H spectra and trichlorofluoromethane (CCl$_3$F) for ^{19}F spectra.

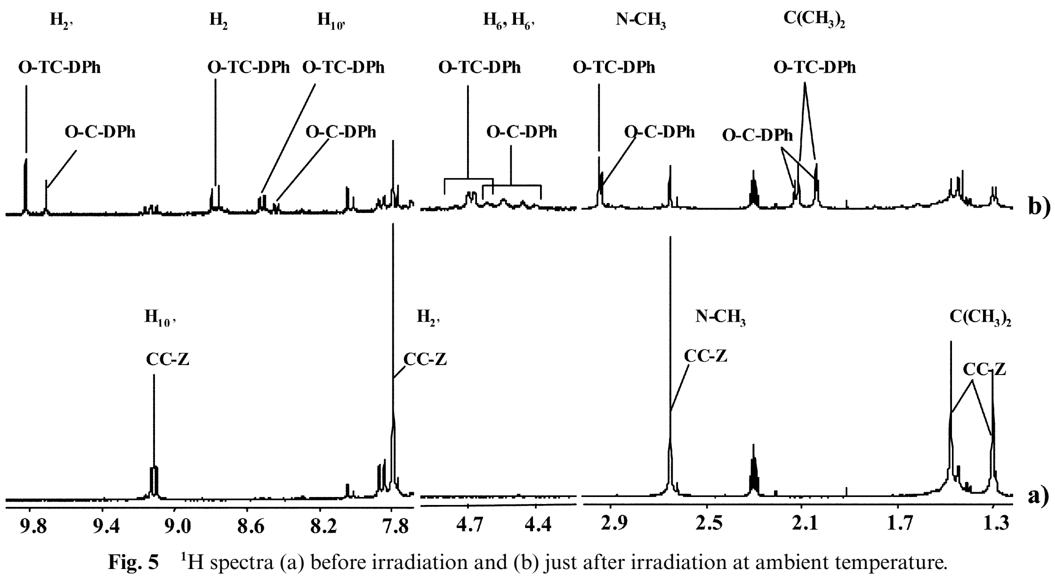
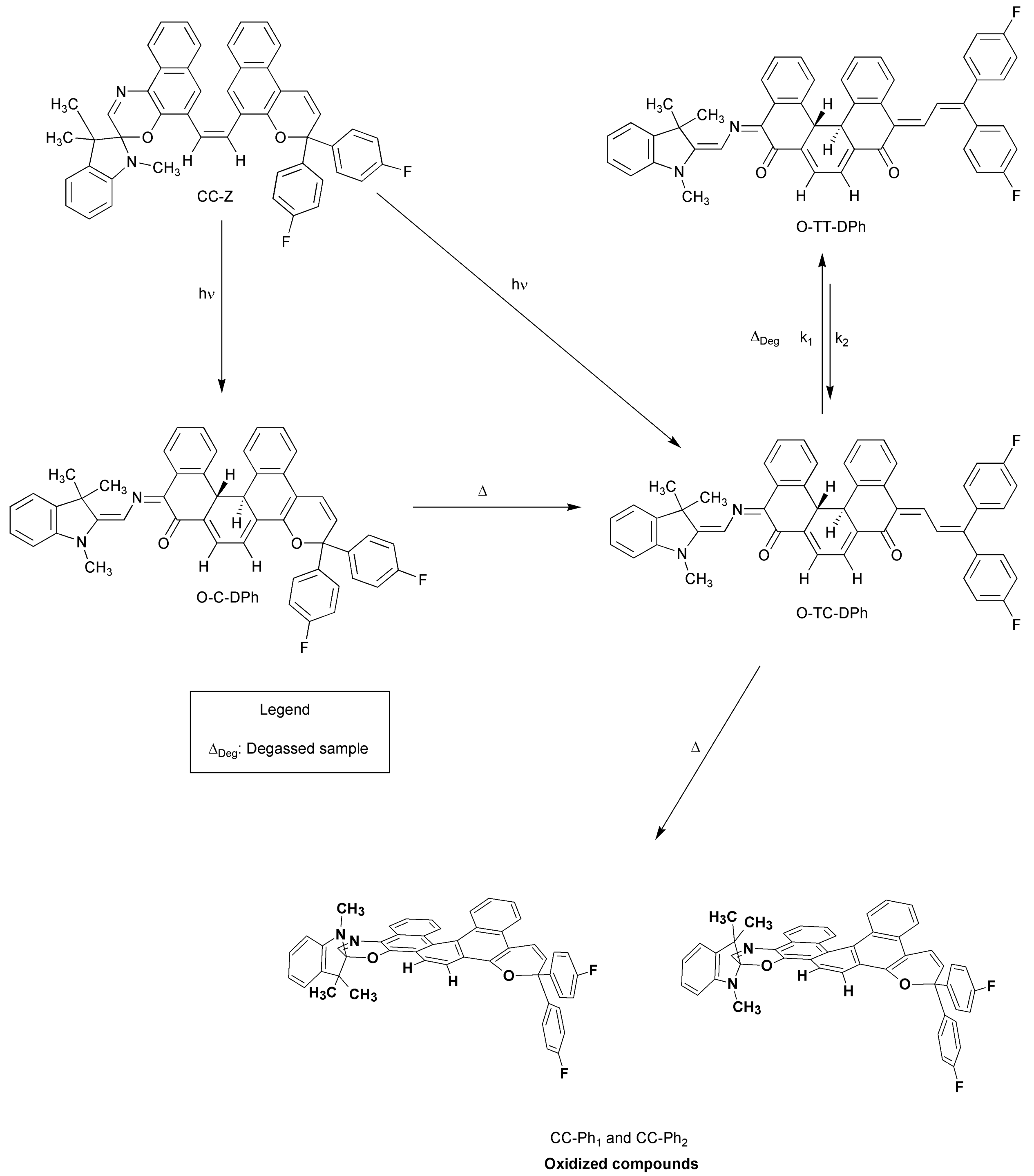


Fig. 5 ^{1}H spectra (a) before irradiation and (b) just after irradiation at ambient temperature.



Scheme 2

Preparation of degassed samples

The degassing of solutions to remove oxygen was carried out by the technique of freeze–pump–thaw cycles (6 cycles) directly in the J. Young valve NMR sample tubes (Wilmad 507-JY-7).

NMR data

CC-*Z*. ^{1}H and ^{19}F NMR (toluene-d$_8$): 1.31(3H, s, CH$_3$); 1.43(3H, s, CH$_3$); 2.66(3H, s, N–CH$_3$); 7.80(1H, s, H-2′); 7.80(1H, s, H-6′); 7.06(1H, d, H-7′); 7.02(1H, dd, J = 6.7 Hz, H-8′); 7.52(1H, dd, J = 6.7 Hz, J = 8.1 Hz, H-9′); 9.11(1H, d, J = 8.1 Hz, H-10′); 7.03(1H, d, J = 7.4 Hz, H-4a); 7.09(1H, dd, J = 7.4 Hz, J = 7.4 Hz, H-5a); 7.29(1H, dd, J = 7.4 Hz, J = 7.8 Hz, H-6a); 6.52(1H, d, J = 7.8 Hz, H-7a); 7.21(1H, d, J = 10.0 Hz, H-1); 5.97(1H, d, J = 10.0 Hz, H-2); 7.80(1H, s, H-6); 7.22(1H, d, H-7); 7.13(1H, dd, J = 8.3 Hz, H-8); 7.36(1H, dd, J = 8.3 Hz, J = 8.5 Hz, H-9); 7.87(1H, d, J = 8.5 Hz, H-10); 7.38(4H, dd, $J_{2''-3''}$ = 9.1 Hz and $J_{2''-F}$ = 5.3 Hz, H-2″); 6.89(4H, dd, $J_{2''-3''}$ = 9.1 Hz and $J_{3''-F}$ = 8.9 Hz, H-3″); 6.91(1H, d, J = 12.3 Hz, H-a); 7.05(1H, d, J = 12.3 Hz, H-b); −113.58(1F, s); −113.65(1F, s)

CC-*Z*. ^{1}H and ^{19}F NMR (acetone-d$_6$): 1.38(6H, s, CH$_3$); 2.73(3H, s, N–CH$_3$); 7.88(1H, s, H-2′); 7.56(1H, s, H-6′); 7.22(1H, d, H-7′); 7.23(1H, dd, J = 6.7 Hz, H-8′); 7.50(1H, dd, J = 6.7 Hz, J = 8.1 Hz, H-9′); 8.54(1H, d, J = 8.1 Hz, H-10′); 7.19(1H, d, J = 7.4 Hz, H-4a); 6.89(1H, dd, J = 7.4 Hz, J = 7.4 Hz, H-5a); 7.22(1H, dd, J = 7.4 Hz, J = 7.8 Hz, H-6a); 6.66(1H, d, J = 7.8 Hz, H-7a); 7.54(1H, d, J = 10.0 Hz, H-1); 6.42(1H, d, J = 10.0 Hz, H-2); 7.43(1H, s, H-6); 7.40-(1H, d, H-7); 7.22(1H, dd, J = 8.3 Hz, H-8); 7.44(1H, dd,

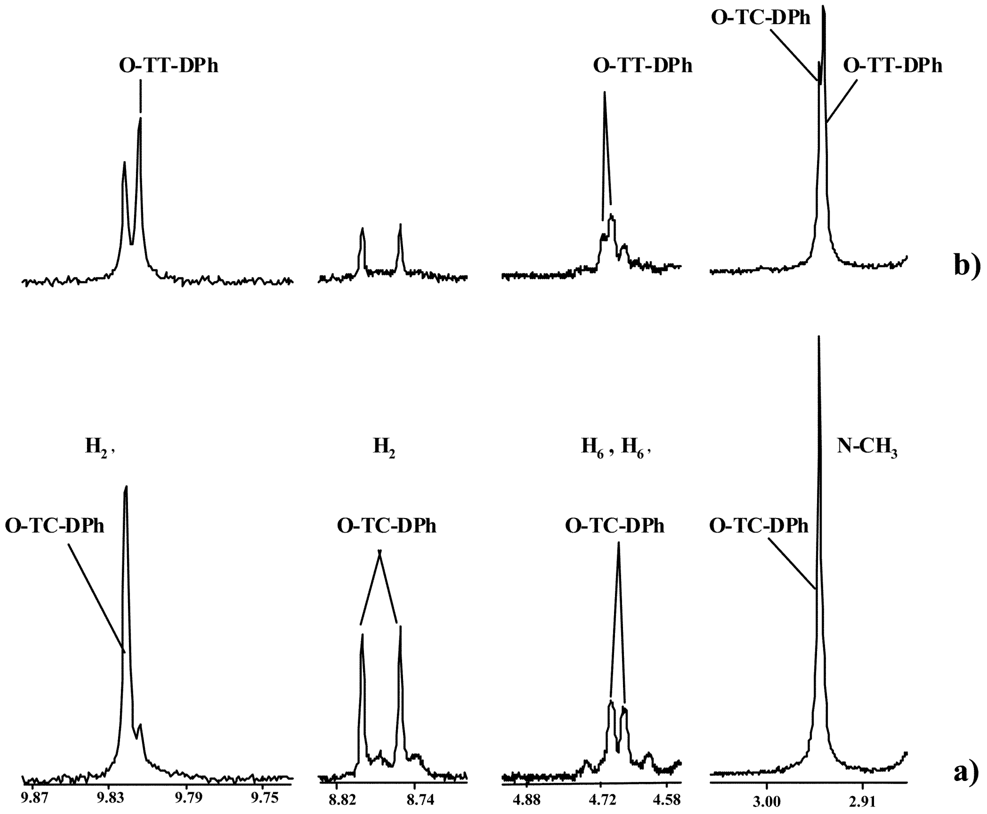


Fig. 7 ^{1}H NMR spectra of the degassed sample at ambient T after irradiation, (a) t = 30 min and (b) t = 12 h.

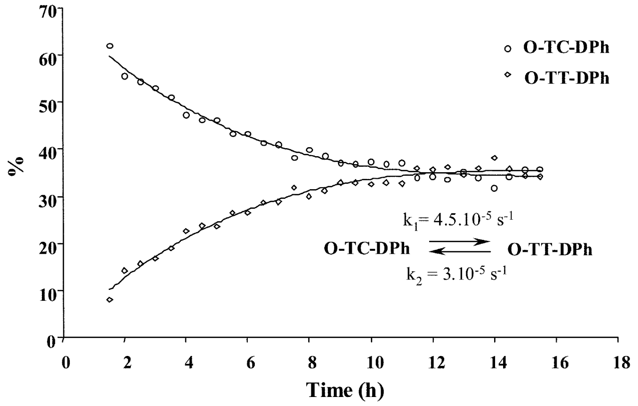
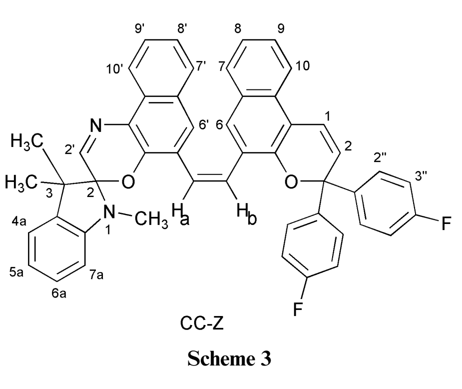


Fig. 8 Thermal equilibrium between **O-TC-DPh** and **O-TT-DPh** in the degassed sample.



Scheme 3

J = 8.3 Hz, J = 8.5 Hz, H-9); 8.07(1H, d, J = 8.5 Hz, H-10); 7.46(4H, dd, $J_{2''-3''}$ = 9.1 Hz and $J_{2''-F}$ = 5.3 Hz, H-2″); 7.02(4H, dd, $J_{2''-3''}$ = 9.1 Hz and $J_{3''-F}$ = 8.9 Hz, H-3″); 6.80(1H, d, J = 12.3 Hz, H-a); 6.99(1H, d, J = 12.3 Hz, H-b); −115.54(1F, s); −115.61(1F, s)

CC-*E*. ^{1}H and ^{19}F NMR (acetone-d$_6$): 1.39(3H, s, CH$_3$); 1.41(3H, s, CH$_3$); 2.83(3H, s, N–CH$_3$); 7.94(1H, s, H-2′); 8.02(1H, s, H-6′); 7.87(1H, d, J = 8.1 Hz, H-7′); 7.47(1H, dd, J = 8.1 Hz, J = 6.9 Hz, H-8′); 7.58(1H, dd, J = 6.9 Hz, J = 8.6 Hz, H-9′); 8.56(1H, d, J = 8.6 Hz, H-10′); 7.19(1H, d, H-4a); 6.89(1H, dd, J = 7.5 Hz, H-5a); 7.22(1H, dd, J = 7.5 Hz, J = 7.9 Hz, H-6a); 6.66(1H, d, J = 7.9 Hz, H-7a); 7.54(1H, d, J = 9.9 Hz, H-1); 6.49(1H, d, J = 9.9 Hz, H-2); 7.41(1H, s, H-6); 7.70(1H, d, J = 8.0 Hz, H-7); 7.37(1H, dd, J = 8.0 Hz, J = 6.8 Hz, H-8); 7.48(1H, dd, J = 6.8 Hz, J = 8.1 Hz, H-9); 8.05(1H, d, J = 8.1 Hz, H-10); 7.58(4H, dd, $J_{2''-F}$ = 5.3 Hz, H-2″); 7.10(4H, dd, $J_{3''-F}$ = 8.9 Hz, H-3″); 7.70(1H, d, J = 16.5 Hz, H-a); 7.77(1H, d, J = 16.5 Hz, H-b); −115.37(1F, s); −115.44(1F, s)

Acknowledgements

The 300 MHz NMR facilities were funded by the Région Nord-Pas de Calais (France), the Ministère de l'Education Nationale, de l'Enseignement Supérieur et de la Recherche (MENESR) and the Fonds Européens de Développement Régional (FEDER).

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