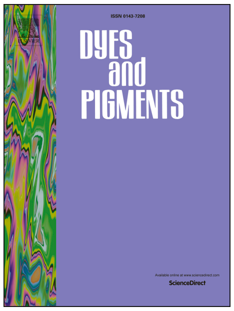

A closer look at the photochromism of vinylidene-naphthofurans

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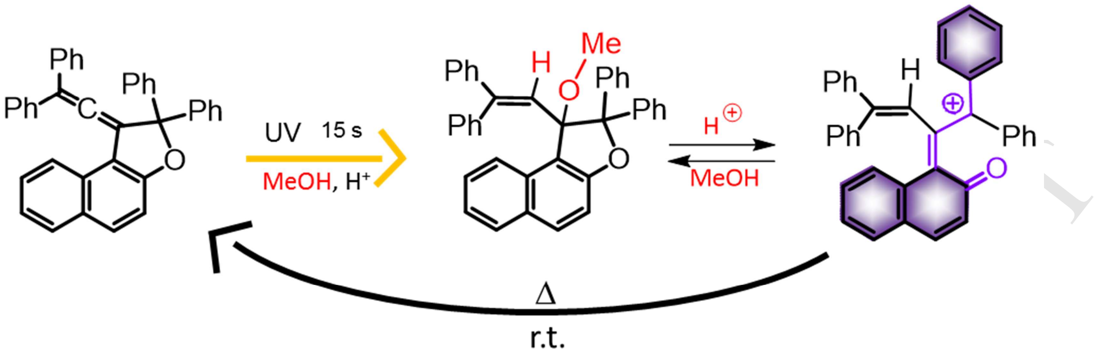
GRAPHICAL ABSTRACT



A closer look at the photochromism of vinylidene-naphthofurans

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ABSTRACT

Vinylidene-naphthofurans are a new class of photochromic molecules, easily synthetized, with a unique structure combining an allene group linked to a dihydrofuran ring. These uncoloured molecules show acidochromism in solution and photochromic properties when adsorbed in silica gel or dissolved in acidified alcoholic solutions but not in common solvents or in the solid state. A mechanism for their thermally reversible photochromic behaviour is proposed based on NMR analysis of UV-irradiated CH_3OD + THF-d8 acidified solutions: the UV light promotes the addition of methanol to the naphthofuran affording a set of non-coloured photoproducts which evolve towards a non-coloured compound P_2. In the presence of acid, the later is quickly converted into a cationic violet dye that returns thermally to the initial closed naphthofuran in the dark. This photochromic system switches between the uncoloured and violet state after UV or sunlight exposure (15 s) and returns thermally to the initial uncoloured state in 2-8 min, in the dark, at room temperature.

Keywords: Naphthofuran, silica gel, photochromism, ring-opening, thermal stability, acidochromism, photoswitches, UV light, NMR.

Highlights:

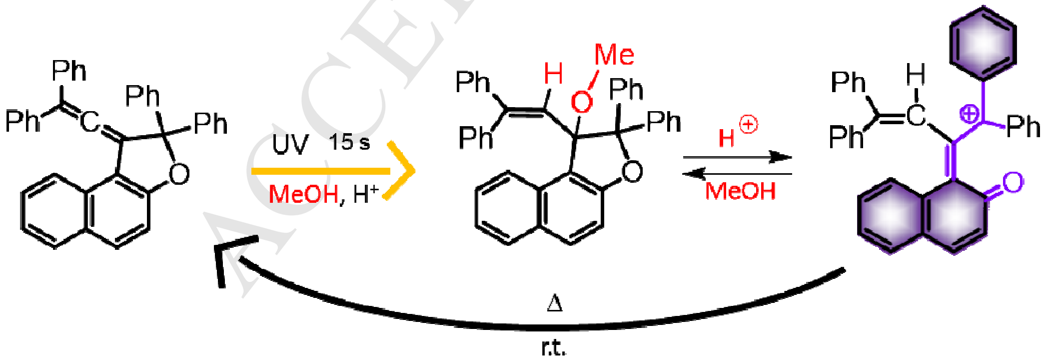
New photochromic vinylidene-naphthofurans were easily synthesised from 2-naphthol.

The naphthofurans show acidochromic properties and photochromic behaviour in acidified methanolic solutions and when adsorbed in silica gel.

This photochromic system works at room temperature switching between the uncoloured and violet state.

A mechanism for their photochromic behaviour is proposed based on NMR analysis.

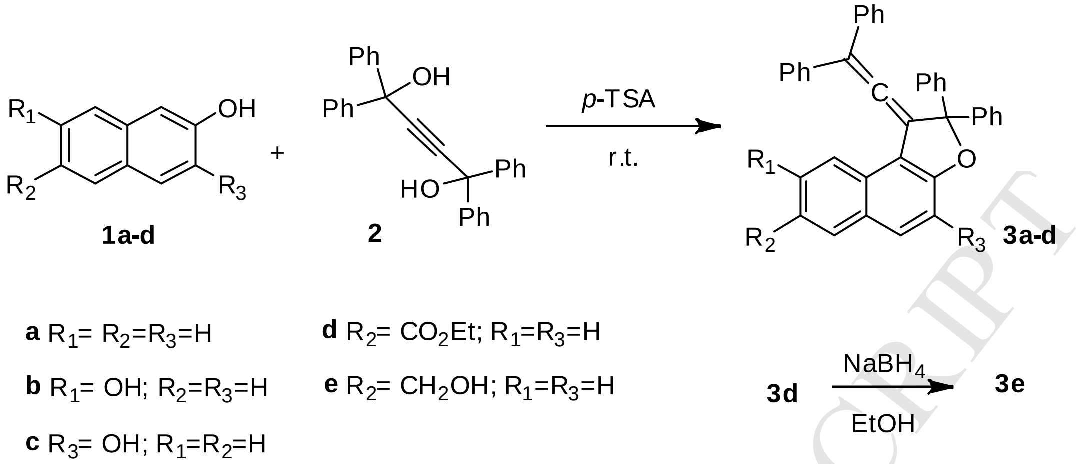
GRAPHICAL ABSTRACT



1. INTRODUCTION

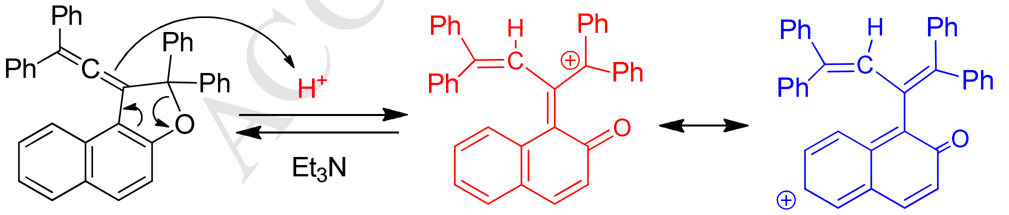
Photochromic compounds are commonly uncoloured molecules that upon irradiation with UV light develop an intense colouration due to an intramolecular photochemical reaction which affords one or more highly conjugated species with a strong absorption in the visible spectrum [1] These coloured photoisomers return to the initial uncoloured form either thermally, in the dark, or upon irradiation with visible light [2] There are many classes of photochromic molecules that exhibit this phenomenon in solution or when the molecules are dispersed in polymeric matrices [3]. More rarely, some molecules can also undergo reversible colour changes in the solid state under the action of light [4]. Some of the most common intramolecular photochemical reactions involved in this phenomenon include heterolytic bond breaking (spirooxazines, naphthopyrans, spiropyrans) [5] or bond forming (diarylethenes) [6], *cis-trans* isomerizations (azo compounds) [7] and intramolecular hydrogen transfer (anil schiff bases) [8]. Some of these compounds, with thermally reversible photochromic behaviour at room temperature, have been applied with commercial success on optical devices like ophthalmic lenses [9] while those who require light activation in both directions have potential applications in memories [10] and as switches to control complex biological systems [11].

We have recently discovered a new type of photochromic molecules with a 1-vinylidene-naphtho[2,1-*b*]furan structure [12]. These uncoloured molecules are easily prepared by acid catalysed reaction of 2-naphthols with readily available tetraarylbut-2-yn-1,4-diols at room temperature (compound **3a**, Scheme 1) and show a particular photochromic behaviour: they are not photochromic in common organic solvents (THF, Et_2O, $CHCl_3$, CH_2Cl_2, DMSO, Toluene) at room or low temperature, nor the solid state, or when dispersed in PMMA polymers, but undergo a rapid colour change when dispersed in silica gel and exposed to the UV or sunlight, affording a violet material that fades in the dark in few minutes. This process is reversible and can be repeated several times without noticeable degradation.



Scheme 1. Synthesis of 1-vinylidene-naphtho[2,1-*b*]furans **3a-e**.

These molecules show also acidochromic properties: in strong acidic medium (CF_3COOH in $CHCl_3$) the 1-vinylidene-naphtho[2,1-*b*]furans are converted into stable cationic species that exhibit two absorption maxima at around 450 and 580 nm and bleach back to the uncoloured closed form upon neutralisation with Et_3N. The structure of these dyes was determined by NMR analysis which confirmed the addition of one proton to the allene function with opening of the furan ring and formation of a tertiary carbocation (Scheme 2).



Scheme 2. Acidochromism of 1-vinylidene-naphtho[2,1-*b*]furan **3a** in $CHCl_3$.

The fact that these compounds are active on the surface of silica gel, but not when dispersed in quartz (SiO_2) suggests that the presence of polar OH groups is essential for the stabilization of the coloured species. Moreover the species obtained after acid addition seem to be similar to the ones formed on the silica surface.

To clarify the nature of the coloured species of this photochromic system, we decided to prepare a series of new substituted naphthofurans substituted by phenolic or aliphatic OH groups (**3b-e**, Scheme 1) and test their behaviour in silica gel and in solution, with the aim to find the right conditions allowing to activate their photochromism in solution. In that way, alcoholic solutions were envisaged, however, since these compounds are not soluble in pure methanol, THF were used as a co-solvent (CH_3OH/THF 4/1).

Although the UV-Vis spectroscopy is the main technique to study photochromism, as it allows to get useful mechanistic information such as the maximal absorption wavelength, molar extinction coefficient and fading rate constants, when more than one species are formed this method becomes unsatisfactory. Despite its poor time resolution, NMR spectroscopy has developed, in the last decade, into a powerful tool in the study of photochromism [13]. Not only it is possible to identify the number, concentration and structure of the chemical species formed after irradiation, using essentially 2D-techniques, but one can also follow their time evolution. For less stable species it is possible to perform all the analysis at low temperature, thus increasing their lifetime [14]. Therefore to fully characterize a photochromic system a combination of both UV-Vis and NMR spectroscopy are needed. In this paper we use these two techniques to investigate the mechanism of the photochromism of 1-vinylidene-naphtho[2,1-*b*]furans in silica gel and in acidified alcoholic solutions.

2. RESULTS AND DISCUSSION

2.1 Synthesis and characterization

A set of four substituted 1-vinylidene-naphtho[2,1-*b*]furans **3a-d** were prepared by reaction of naphthols **1a-d** with 1,1,4,4-tetraphenylbut-2-yn-1,4-diol **2** in $CHCl_3$, in the presence of a catalytic amount of *p*-toluenesulfonic acid, at room temperature (37-49% yield) (Scheme 1) [12]. The straightforward formation of these allenic derivatives shows that this reaction is compatible with the presence of other reactive organic functions in the initial naphthol, such as esters or alcohols. Reduction of the ester function of naphthofuran **3d** with $NaBH_4$ in ethanol gave the corresponding alcohol **3e**, in good yield (82%), without any perturbation of the dihydrofuran cycle.

Besides the expected aromatic signals in the ^1H NMR spectrum, these compounds show two distinctive signals in the ^{13}C NMR spectrum: a low field signal around 202 ppm, characteristic of the allene function, and a signal at 95 ppm assigned to the dihydrofuran sp^3 carbon atom. A mechanism for this one-pot reaction was previously proposed [12].

2.2. Acidochromic properties

All the compounds **3a-e** showed acidochromic properties. Addition of TFA to a $CHCl_3$ uncoloured solution ($1x10^{-4}$ M) of compound **3d** leads to the appearance of a violet colour, characterized by two absorption bands in the visible spectrum (λ_{max}= 425 and 590 nm) that bleached when Et_3N was added to the solution (Figure 1, see supplementary data for other compounds). The process is reversible and upon subsequent addition of acid the violet coloration appears again although the intensity of the bands are a little bit lower which may indicate some degradation of the initial molecule. The same general reversible behaviour was observed with the other vinylidene-naphthofurans (Table 1).

The observed colour change is due to an addition of H^+ to the allene function with opening of the furan ring and formation of a tertiary carbocation (Scheme 2). The band around 425-451 nm resembles the absorption band of a merocyanine dye (open form of the naphthopyran) while the second maxima, between 540-590 nm, may be justified by the extension of the conjugation between the merocyanine and the carbocation. The presence of the hydroxyl substituents in the naphthofuran structure, especially in the 8 position (compound **3b**), led to a significant hypsochromic shift of the λ_{max} of the coloured form.

Table 1. Maxima wavelength of absorption of naphthofurans **3a-e** (1.0×10^{-4} M, $CHCl_3$) before and after TFA addition.

Naphthofuran	**λ_{max} (nm) in $CHCl_3$**	**λ_{max} (nm) - after TFA addition**
3a (H)	373	451 , 580
3b (R_1 = OH)	364	437 , 540
3c (R_3 = OH)	355	448 , 562
3d (R_2 = COOEt)	371	425 , 590
3e (R_2 = CH_2OH)	376	449 , 581

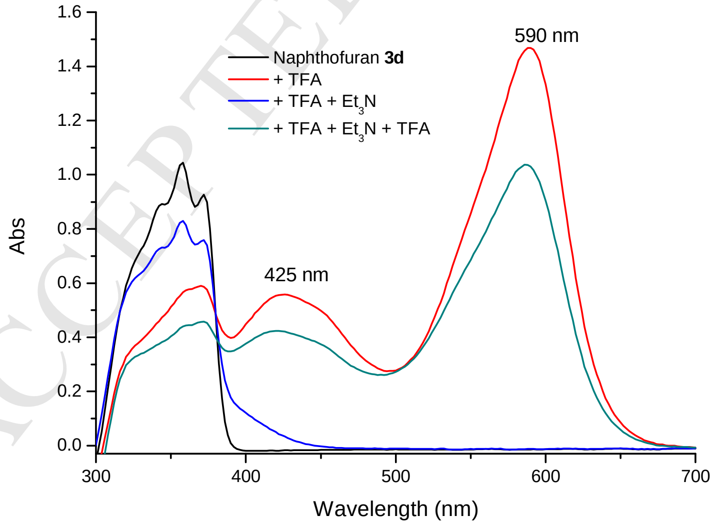


Figure 1. Absorption spectra of a) Naphthofuran **3d** ($CHCl_3$); b) after the addition of TFA; c) followed by addition of Et_3N; d) followed by another addition of TFA.

2.3. Photochromic properties in silica gel

The 1-vinylidene-naphtho[2,1-*b*]furans **3a-e** are uncoloured compounds in $CHCl_3$ solution with a strong absorption in the UV region between 330-380 nm but do not exhibit photochromic properties when exposed to the sunlight or irradiated with UV light (254 or 365 nm). However, when silica gel was added to CH_2Cl_2 solutions of 1-vinylidene-naphthofurans **3a-e** and the solvent removed by evaporation at atmospheric pressure, a white powder of doped silica gel was obtained which turned violet when exposed to UV light/sunlight for 15 s (see video 1_SI) (Figure 2). The phenomenon is only observed after all the solvent is removed and, after UV activation, the addition of any solvent leads to the immediate disappearance of the coloured species.

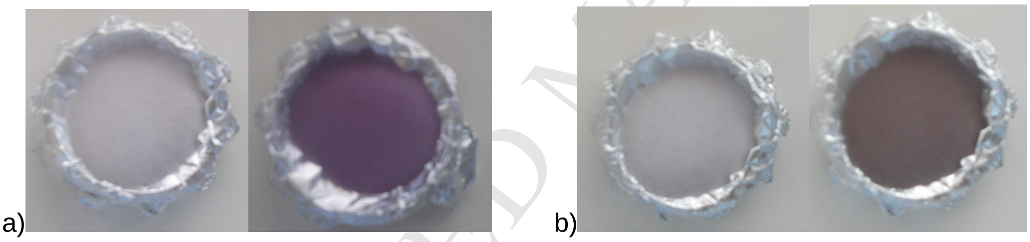


Figure 2. Photographs of silica gel doped with compounds a) **3e** and b) **3b** before and after UV irradiation (6W, 365 nm) for 15 s.

The absorption spectra of the doped silica gel materials, before and after UV irradiation, can be determined using a UV-Vis spectrometer equipped with an external Diffuse Reflectance accessory that measures the diffuse reflected light: before UV irradiation, the silica gel doped with compounds **3a-e** is white with a very low absorption in the visible spectrum. After exposure to the UV light (6W, 365 nm, 15 s) the samples acquire a violet colouration characterized by a broad absorption in the visible spectra with two maxima: one around 440-450 nm and the second, more intense, around 530-570 nm (Figure 3, table 2), except for compound **3b** which exhibited a brown colour characterized by two maxima at 503 and 690 nm. The fact that, the visible spectra observed upon acid addition (acidochromism) is similar to that measured after UV exposure of these compounds in silica (except for compound **3b**), suggests that the same species is being formed in both situations and therefore, in silica gel, the UV irradiation may also lead to the addition of one proton to the allene with cleavage of the C-O bond and formation of a conjugated cationic species, probably stabilized by the polar OH terminal groups of the silica gel.

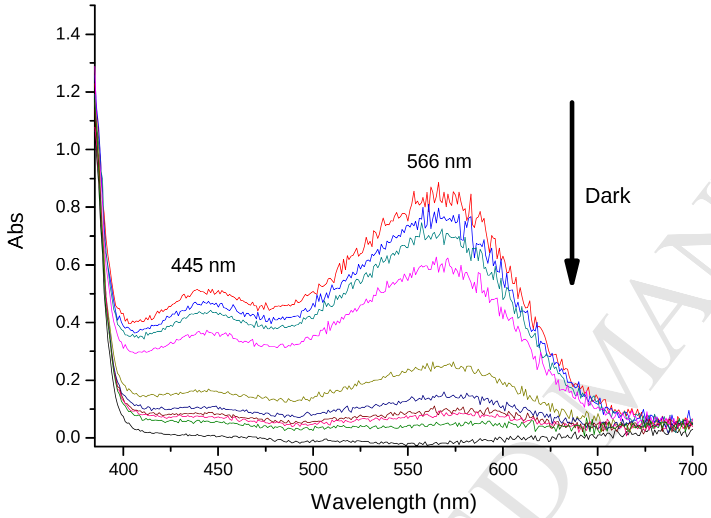


Figure 3. Time-evolution of the UV-Vis spectra of compound **3e** in silica gel during the thermal fading.

Table 2. Absorption maxima of silica gel doped with compounds **3a-e** after UV exposure, bleaching rate constants and half-life time.

Naphthofuran	**λ_{max} (nm) (coloured form)**	**$K_{1\Delta}$ (min^{-1})**	**$K_{2\Delta}$ (min^{-1})**	**$t_{1/2}$ (min)**
3a (H)	442, 562	2.13 (63%)	0.60 (37%)	0.54
3b (R_1 = OH)	503 , 690	0.012	-	57
3c (R_3 = OH)	443 , 528	1.1 (56%)	0.10 (44%)	1.3
3d (R_2 = COOEt)	444 , 569	0.69 (80%)	0.20 (20%)	1.3
3e (R_2 = CH_2OH)	445 , 566	1.44 (53%)	0.45 (47%)	1.3

After ceasing the UV exposure all the samples lose gradually the colouration, returning to the initial white colouration (see video 2_SI). The colour decay of compounds **3a,c-e** is best described by a bi-exponential kinetic model comprising two very different rate constants being the slowest around 3-10 times lower than the fastest. As a result, after an initial fast decay with an half-life time between 0.54 and 1.3 min there is some residual colouration, due to the slowest rate constant, that persists for several minutes. This behavior does not indicate necessarily the presence of several chemical species; in fact it can be due to the existence of different chemical environments on the silica gel material (Table 2, Figure 4). From a practical point of view, this set of compounds return to the uncoloured state in 2-8 min. The colour decay of compound **3b,** with a hydroxyl group in the 8-position of the naphthalene ring, could be fitted to a monoexponential equation with a high half-life time of 57 min at room temperature indicating a much higher stability of the coloured species.

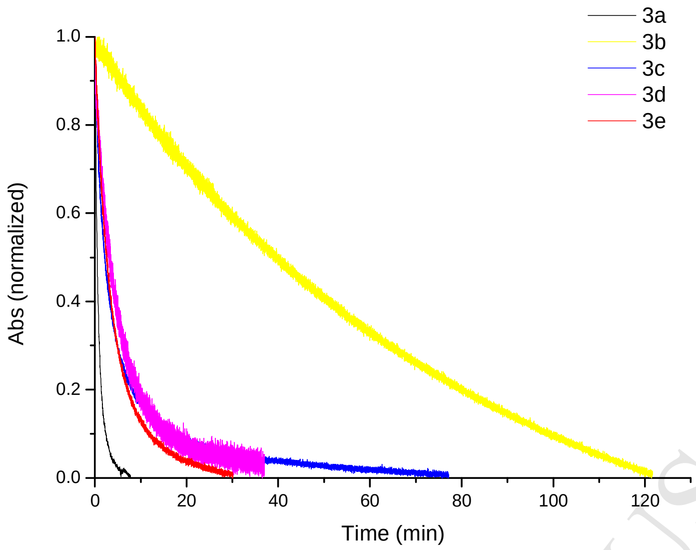


Figure 4. Normalized thermal fading kinetics of silica gel doped with compounds **3a-e** in the dark.

2.4. Photochromic properties in solution

1-Vinylidene-naphthofurans **3a-e** are not photochromic in common organic solvents like THF, Et_2O, EtOAC, $CHCl_3$, CH_2Cl_2, DMSO or Toluene. However, the addition of small amounts of a strong acid like H_2SO_4, HNO_3, H_3PO_4 or citric acid to a solution of compounds **3a-c,e** in THF/CH_3OH followed by irradiation with UV or sunlight allows to observe a reversible colour change. The visible spectra of the solution shows the appearance of the same two bands observed upon acid addition (acidochromism) and in silica gel, suggesting that the same species is being formed in these three different conditions (Figure 5). The same visible spectra is observed regardless of the added acid, however, a solution of these compounds in HOAc remains uncoloured under UV. Therefore, the presence of methanol and a small quantity of a strong acid are essential. The THF plays the role of co-solvent as the compounds are not soluble in methanol. Only for compound **3d** a noticeable colour change was not observed under these conditions probably due to a higher switching speed which leads to a lower concentration of the opened forms.

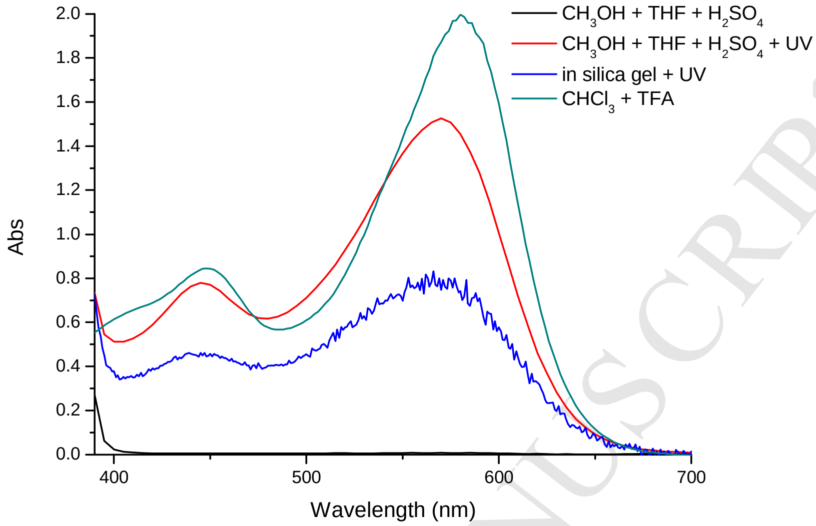


Figure 5. UV-Vis spectra of compound **3e:** a) in THF + methanol + H_2SO_4 before irradiation b) in silica after UV irradiation c) in THF + methanol + H_2SO_4 after UV light exposure d) in $CHCl_3$ + TFA.

After ceasing the UV exposure the solutions of compounds **3a-c,e** lose gradually the coloration, returning to the initial colouration following a mono-exponential decay. The fading kinetics of the coloured species observed in these conditions are all similar but much slower ($t_{1/2} \approx 21$ min) than the ones observed in silica gel indicating a much higher stability of the photoproducts in methanolic solutions. The compounds showed also photochromic properties in acidified ethanol although the colour intensity and the fading kinetic were lower. The photochromic behaviour of these compounds in methanol/THF solutions created the opportunity to study the mechanism of this photochemical reaction by NMR in CH_3OD+THF-d8 solutions.

2.5. NMR studies on 1-vinylidene-naphthofuran ***3b***

NMR investigations were carried out to identify the structure of the colored species obtained after UV irradiation of compound **3b** in an acidic solution of CD_3OD + THF-d8 (see supplementary data for details). The studies were conducted using this compound because it affords colored species with high thermal stability and the co-solvent THF-d8 was used because these compounds show a limited solubility in methanol.

UV irradiation of **3b** in a solution of MeOD-d_4, THF-d_8 and TFA at room temperature led to the formation of two new products, P_1 and P_2 (Figure 6), in a ratio depending on the acid amount. A low amount of acid favors P_2 while the equilibrium is shifted towards P_1 upon further acid addition, so P_1 is formed from P_2 (see SI). In the dark, the photoproducts P_1 and P_2 return thermally to the initial compound **3b**. 1D and 2D NMR analysis allowed to identify the structures of P_1 and P_2 (Scheme 3). More particularly, in P_1, the protons H-2" and H-2"a are equivalent due to the presence of a carbocation at C-4, while H-2' and H-2'a resonate at very different chemical shifts (6.72 and 7.40 ppm). Proton H-2' is shifted upfield at 6.72 ppm probably due to an anisotropic effect. The C=O function in P_1 is clearly underlined by the long-range scalar correlation between proton H-6 at 8.56 ppm and carbon C-4a at 183.8 ppm measured by ^{1}H-^{13}C HMBC experiment recorded at -5°C to slow down the thermal relaxation.

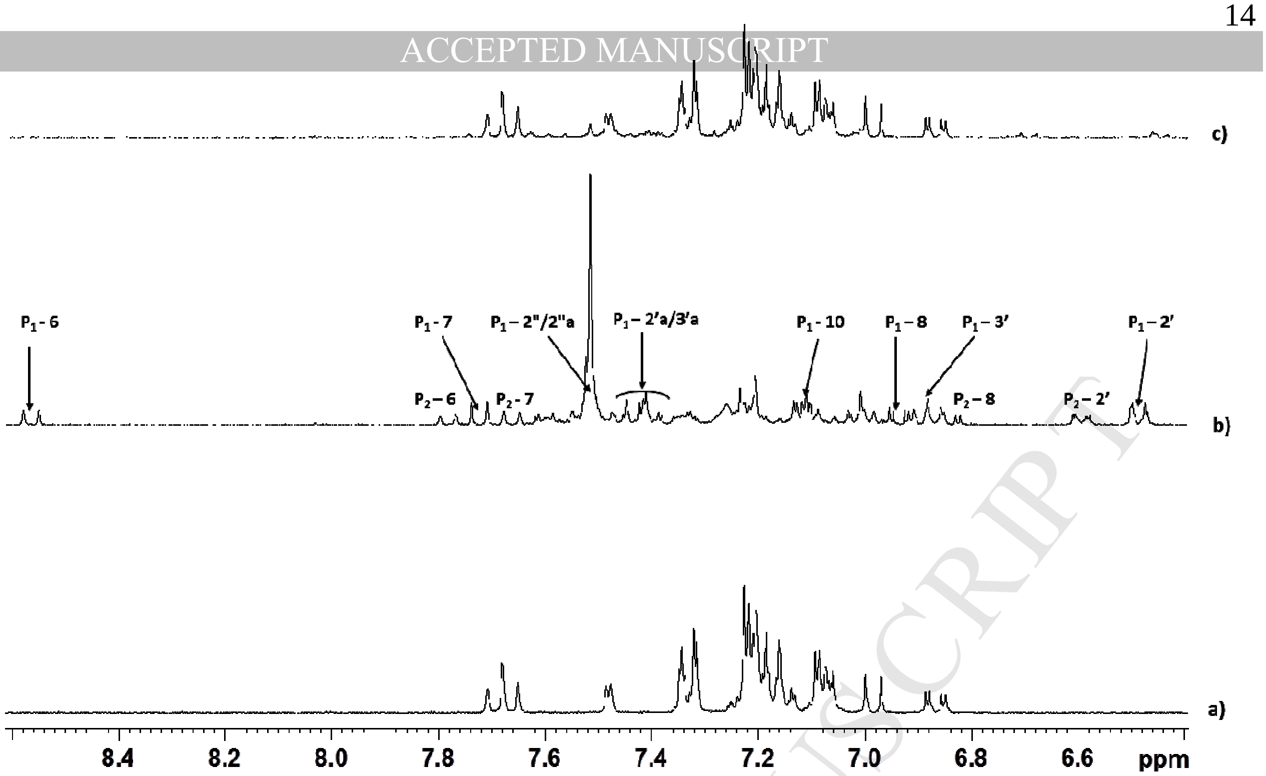
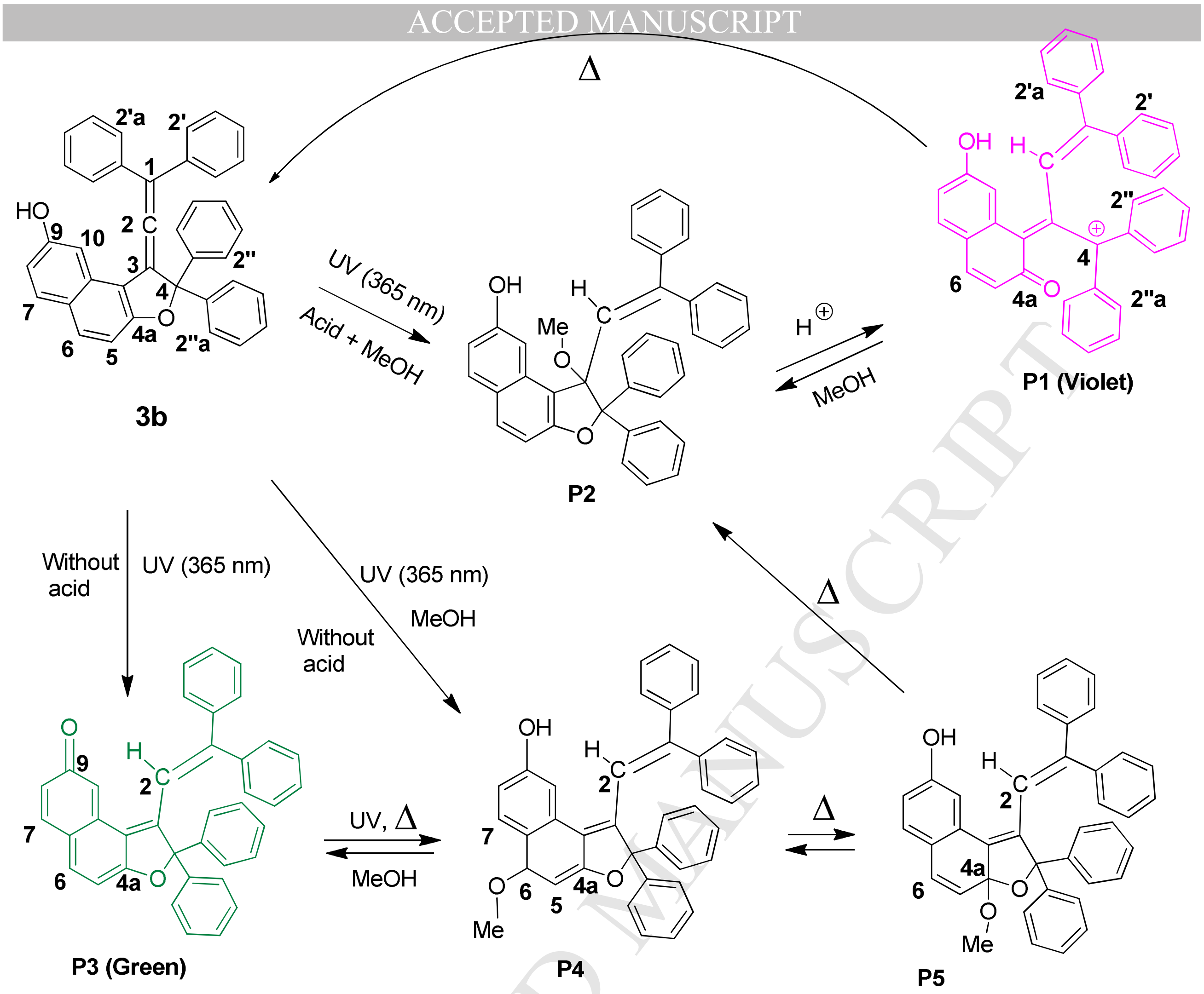


Figure 6. NMR spectra of naphthofuran **3b** in CD_3OD + THF-d_8 +TFA a) before irradiation, b) after 30 min of UV irradiation at 365 nm and c) after two days of thermal evolution.



Scheme 3. Mechanism of photochromism for 1-vinylidene-naphthofuran **3b.**

Contrary to P_1 which has an opened structure, P_2 maintains the dihydrofuran ring structure but has a methoxy substituent at carbon C-3. This was nicely confirmed by repeating the experiment using protonated instead of deuterated methanol and by recording the ^{1}H-^{13}C HMBC spectra which evidenced long-range correlations between C-3 at 93.0 ppm and protons H-2 at 5.77 ppm and O-CH_3 at 2.12, as well as between C-4 at 98.0 ppm and the aromatic protons H2” and H2”a at 7.4 and 7.6 ppm, respectively.

UV irradiation of a fresh solution of **3b,** without trace of acid, in a mixture of CD_3OD and THF-d8, led to the formation of three other photoproducts, P_3, P_4 and P_5 (Scheme 3, Figure 7) which evolved over several days in the dark towards the previously identified product P_2. Acidification of this solution, containing P_2, afforded a violet coloration, characteristic of P_1 which in turn evolved thermally towards the initial naphthofuran **3b**.

To characterize P_3, P_4 and P_5, the experiment was repeated at -20℃ to slow down their thermal relaxation. Decreasing the temperature allowed to firstly accumulate P_3 and P_4, and then P_4 slowly equilibrated with P_5.

P_3 is formed by intramolecular proton transfer from the phenolic group at C-9 to the allene carbon C-2 which affords a conjugated naphthofuranone derivative displaying a green coloration. In the ^1H-^{13}C HMBC experiment, long range correlations between proton H-7 at 7.31 ppm and the carbonyl carbon C-9 at 183.5 ppm and between the proton H-6 at 7.68 ppm and the carbon C-4a at 173.4 ppm were observed.

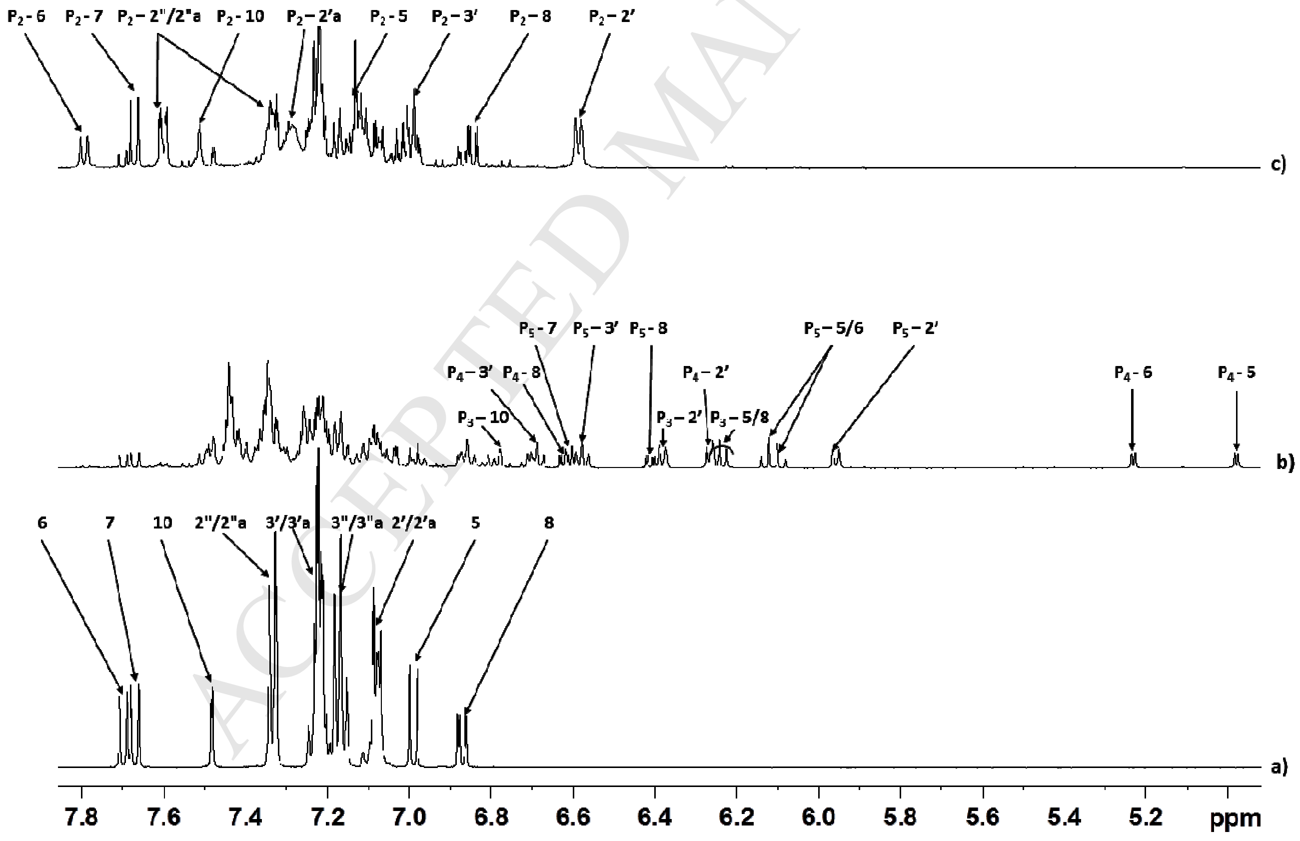


Figure 7. NMR spectra of naphthofuran **3b** in CD_3OD + THF-d_8 a) before irradiation, b) after 40 min of UV irradiation at 365 nm and c) after several days of thermal evolution.

P_4 is produced by a [1,6] photoaddition of methanol to position 6 of the naphthalene ring and protonation of the allene carbon C-2. The ^1H-^{13}C HMBC experiment, recorded at -60℃, in a mixture of protonated methanol and THF-d_8, allowed to correlate the aromatic proton H-7 at 7.00 ppm and the protons of the methoxy group at 2.22 ppm with the carbon C-6 at 73.4 ppm, the proton H-6 at 5.27 ppm with the carbon C-5 at 89.0 ppm, and finally, the protons H-6 at 5.27 ppm and H-5 at 4.9 ppm with the carbon C-4a at 162.3 ppm.

P_5 is obtained by thermal [1,3] shift of the methoxy group from C-6 to C-4a, as proved by scalar correlations between C-4a at 108.0 ppm and the methoxy group at 2.81 ppm and the proton H-6 at 6.08 ppm.

Consequently, and as summarized in Scheme 3, UV irradiation of an acidified methanolic solution of **3b** leads to product P_2, formed by methanol addition to the allene. In the presence of acid this compound establishes a chemical equilibrium with the conjugated carbocation P_1, responsible for the violet coloration of the solution and the main photoproduct in these acidic conditions. This dye then reverts thermally directly to the initial naphthofuran closing the photochromic cycle.

This three-state system can also be reached through irradiation of a methanolic solution of **3b** without acid trace. In this case, **3b** is converted into the coloured naphthofuranone derivative P_3, formed by intramolecular proton transfer, and two uncolored compounds P_4/P_5 formed through methanol addition to the naphthalene ring. P_3 and P_4 are the initial photoprodutcs and then they are thermally converted into P_5 and then to P_2, which, in the absence of acid, is very stable. Addition of acid to a solution constituted mainly by P_2 leads to the formation of the coloured P_1 that evolves thermally towards the initial **3b.**

This mechanism was also confirmed for the unsubstituted naphthopyran **3a** (without the phenolic group), except that the formation of P_3, which involves the participation of the

OH group, was not observed. This is illustrated in the supplementary file with data reported for compound **3a**.

The easiness of the synthesis of these photochromic compounds associated with their sensibility to the sunlight, and the possibility of controlling the colour and the speed of the switching between the two species makes these new compounds promising candidates for application in optical devices where a fast colour switch is demanded. The need for an acidic media and the fact that other photoproducts are formed are not a limitation since the system is reversible in the presence of acid without signs of degradation. However, their incorporation on a transparent material is still a challenge.

3. Conclusions

Vinylidene-naphthofurans exhibit acidochromic properties in TFA solutions and photochromic properties when dispersed in silica gel or dissolved in acidified CH_3OH/ THF solutions. The photochromic properties in solution are due to the addition of methanol to the naphthofuran affording a set of photoproducts that evolve towards compound P_2, which in the presence of acid is quickly converted into a cationic violet dye that returns thermally to the initial closed naphthofuran compound in the dark at room temperature. The structure of this cationic violet dye is the same as the one obtained upon addition of the strong trifluoroacetic acid. White silica-gel doped with compounds **3a-e** acquires also a violet colour after UV or sunlight exposure, affording very likely the same coloured species, which returns thermally in the dark to the uncoloured state in 2-8 min.

4. EXPERIMENTAL SECTION

4.1 General Methods

All reactions were monitored by thin-layer chromatography on aluminium plates coated with Merck silica gel 60 F254 (0.25 mm). ^{1}H and ^{13}C NMR spectra were recorded at 298 K on a Bruker ARX400 spectrometer (at 400.13 and 100.62 MHz). The new compounds were determined to be >95% pure by 1H NMR spectroscopy. IR spectra were obtained on a Unicam Research Series FTIR spectrometer using KBr pellets. Wavenumbers (λ_{max}) are reported in cm^{-1}. UV-Vis spectra were recorded on a Cary 50 Spectrophotometer. High resolution electrospray ionization time-of-flight (ESI-TOF) mass spectra and electron impact time-offlight (EI-TOF) mass spectra were measured with a VG AutoSpec M spectrometer. Melting points were determined in open capillary tubes in a Buchi 535 melting point apparatus and are uncorrected. 1,1,4,4-Tetraphenylbut-2-yn-1,4-diol **2** and 1,2-dihydro-1-(2,2-diphenyl)vinylidene)-2,2-diphenylnaphtho-[2,1-*b*]furan **3a** were prepared using published methods.[12]

4.2. Synthesis

*4.2.1. Synthesis of naphthofurans **3b-d**. General procedure:* To a solution of naphthol and 1,1,4,4-tetraphenylbut-2-yn-1,4-diol **2** (1 eq.) in $CHCl_3$ (15 mL) was added 4-toluenesulfonic acid monohydrate (catalytic). The solution was stirred at room temperature for 1-24 hours. After water addition (40 mL), the organic phase was separated and the aqueous phase extracted with $CHCl_3$ (3x25 mL). The organic phase was dried (Na_2SO_4) and the solvent removed under reduced pressure affording an oil that was purified by column chromatography on silica gel and/or recrystallization.

*4.2.2. 8-Hydroxy-1-(2,2-diphenylvinylidene)-2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan **3b**.* Prepared from 2,7-dihydroxynaphthalene (500 mg; 3.12 mmol) and diol **2** (1.218 g, 3.12 mmol). The product was purified by column chromatography (10% ethyl acetate/petroleum ether) and recrystallization from CH_2Cl_2/petroleum ether. Obtained as off-white crystals (707 mg, 44%). **mp** 229-231 ºC. **IR (KBr, cm^{-1})**: 3594, 3487, 3253, 3060, 1623, 1487, 1452, 1245, 1203, 833, 762, 697. **^{1}H NMR** (300 MHz,$CDCl_3$): 7.74 (d, J=9.3 Hz, 2H), 7.52 (d, J=2.4Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): 202.53, 158.50, 155.26, 142.94, 136.39, 131.70, 131.16, 131.13, 128.68, 128.46, 128.12, 127.88, 127.75, 127.30, 125.37, 117.34, 115.18, 114.97, 112.04, 109.88, 104.79, 94.81. **EI-MS** (TOF) m/z (%): 514 (96), 438 (25), 437 (100), 347 (28), 331 (19), 323 (10), 302 (11), 300 (12), 289 (10) 165 (14). **HRMS** calcd for $C_{38}H_{26}O_2$: 514.1933. Found: 514.1934.

4.2.3 4-Hydroxy-1-(2,2-diphenylvinylidene)-2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan ***3c.*** Prepared from 2,3-dihydroxynaphthalene (250 mg; 1.59 mmol) and diol **2** (620 mg, 1,59 mmol). The product was purified by column chromatography (10-15% ethyl acetate/petroleum ether) and recrystallization from diethyl ether/petroleum ether and obtained as slight yellow crystals (294 mg, 37%). **mp** 216-220 ºC. **IR** (KBr, cm^{-1}): 3416, 3060, 3025, 1601, 1516, 1491, 1470, 1452, 1405, 1283, 1237, 1182, 771,692. **^{1}H NMR** (300 MHz, $CDCl_3$): 8.15-8.25 (m, 1H), 7.70-7.78 (m, 1H), 7.40-7.50 (m, 4H), 7.50-7.20 (m, 15H), 7.10-7.20 (m, 4H), 5.32 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): 202.62, 147.64, 142.42, 140.97, 136.17, 131.20, 128.74, 128.40, 128.19, 128.16, 127.81, 127.74, 127.37, 125.37, 125.03, 124.34, 122.06, 117.65, 114.79, 114.64, 112.73, 96.17. **EI-MS** (TOF) m/z (%): 514 (100), 437 (40), 348 (51), 302 (15), 289 (12), 167 (12). **HRMS** calcd for $C_{38}H_{26}O_2$: 514.1933. Found: 514.1917.

4.2.4. Ethyl 1-(2,2-diphenylvinylidene)-2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan-7-carboxylate ***3d.*** Prepared from ethyl 6-hydroxy-2-naphthoate (200 mg; 0.92 mmol) and diol **2** (1 eq). The solvent was removed under reduced pressure and ethanol was added to afford a suspension of yellow crystals that were filtered. The product was purified by recrystallization from CH_2Cl_2/petroleum ether and obtained as white crystals (261 mg; 49%). mp 192.2-195.3 ºC. **IR** (KBr, cm^{-1}): 3058, 3026, 2981, 1712, 1626, 1468, 1275, 1240, 1185, 1099, 1022, 949, 928, 812, 765, 698, 649. **^{1}H NMR** (400 MHz, $CDCl_3$): 8.57 (s, 1H), 8.27 (d, J=8.76 Hz, 1H), 8.05 (d, J=8.76 Hz,1H), 7.90 (d; J=8.84 Hz,1H), 7.45-7.43 (m, 4H), 7.33-7.14 (m, 13H), 7.12 (m, 4H), 4.40 (q, J=7.10 Hz, 2H), 1.42 (t, J=7.12 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 202.63, 166.70, 159.47, 142.69, 136.21, 133.20, 132.09, 131.91, 129.13, 128.70, 128.43, 128.17, 128.01, 127.83, 127.36, 127.24, 126.97, 125.48, 122.17, 117.66, 114.18, 113.88, 113.27, 95.32, 60.98, 14.37. **EI-MS** (TOF) m/z (%): 570 (100), 493 (50), 464 (14), 420 (25), 403 (24), 379 (10), 375 (10). **HRMS** calcd for $C_{41}H_{30}O_3$:570.2195. Found: 570.2194.

4.2.5. 7-Hydroxymethyl-1-(2,2-diphenylvinylidene)-2,2-diphenyl-1,2-dihydro naphtho[2,1-b]furan ***3e****.* $LiAlH_4$ (65 mg; 1.72 mmol) was added to a solution of naphthofuran **3d** (982 mg; 1.72 mmol) in dry THF at room temperature with constant stirring. After standing for 1 hour, the solution was slowly added to water and a solution of NaOH (50 eq) in 15 mL of water was added. The mixture was stirred at room temperature for 24 hours and then extracted with dichloromethane (20x10 mL). The organic phases were combined, dried (Na_2SO_4) and the solvent was removed under reduced pressure. The product was recrystallized from dichloromethane/petroleum ether and obtained as white crystals (74 mg; 81%). **mp** 232.7-235.3 ºC. **IR** (KBr, cm^{-1}): 3288, 3060, 3025, 2854, 1632, 1596, 1492, 1469, 1442, 1377, 1270, 1255, 1225, 1157, 1044, 1026, 958, 822, 762, 694, 644. **^{1}H NMR** (400 MHz, $CDCl_3$): 8.2 (d, J= 8.6 Hz, 1H), 7.8 (m, 2H), 7.47-7.43 (m, 5H), 7.29-7.20 (m, 13H), 7.14-7.04 (m,4H), 4.79 (d, J=5.8 Hz, 2H). **^{13}C NMR** (100 MHz,$CDCl_3$): 202.73, 157.87, 142.94, 136.39, 136.04, 131.65, 129.98, 129.27, 128.70, 128.37, 128.11, 127.89, 127.71, 127.28, 127.24, 126.79, 122.63, 117.36, 114.71, 113.58, 112.72, 94.86, 65.41. EI-

MS (TOF) m/z (%):582 (100), 526 (18), 513 (19), 451 (52), 435 (42), 403 (15), 391 (13), 361 (34), 345 (27), 315 (30), 302 (18), 165 (17). HRMS calcd for $C_{39}H_{28}O_2$:528.2089. Found: 528.2090.

*4.3. Acidochromism of compounds **3a-e**:*

Trifluoroacetic acid (5-20 drops) was added to a colorless solution of naphthopfuran **3a-e** ($CHCl_3$, $1x10^{-4}$ M, 3 mL), with manual stirring, until an intense color appeared. Then, triethylamine (5-15 drops) was added until the solution turned colorless. Finally, trifluoroacetic acid (15-30 drops) was added again until the solution turned colored again.

4.4. Photochromism of compounds 3a-e in silica:

*4.4.1. Preparation of the silica gel doped with compounds **3a-e**:*

To a solution of compound **3a-e** (5.0 mg) in CH_2Cl_2 (3 mL) was added 1.0 g of silica gel 60 (0.063-0.200 mm). The mixture was stirred for 30 s and kept at room temperature in dark until the complete evaporation of the solvent at atmospheric pressure (1 night).

4.4.2. Spectra measurements before and after UV irradiation:

The samples powder were placed on a teflon support and a Vilber-Lourmat lamp (365 nm, 6W) was positioned over the samples. The UV light was switch on for 15 s during which all samples developed a violet/pink or brown colouration. The UV-Vis spectra of the solid samples, before and after UV irradiation was recorded using a UV-Vis spectrophotometer (CARY 50 Varian) coupled to a diffuse reflectance accessory that allows measuring the UV-Vis spectra of solid samples. Then the light source was removed and the absorbance at λ_{max} recorded over time to measure the fading kinetics of the samples. All measurements were made at 20±1 ºC. The rate constants (*k*1 and *k*2) were calculated by the fitting of the bleaching curves to a bi-exponential decay equation: $A=A_0+A_1\exp(-k_1t)+A_2\exp(-k_2t)$, where k_1 and k_2 are two bleaching constants. A_1 and A_2 the initial absorbance due to each species and A_o the initial absorbance of the sample before UV irradiation.

4.5. Photochromism of compounds 3a-e in acidified MeOH/THF solution.

4.5.1. Preparation of the solution:

5 mg of the naphthofurans **3a-e** were dissolved in 2.0 ml of THF and then 8.0 mL of methanol and 1 drop of conc. sulfuric acid were added. This solution of transferred in to a Quartz UV-vis Cell.

4.5.2. Spectrokinetic studies under continuous irradiation:

UV-visible irradiation experiments were made using a CARY 50 Varian spectrometer coupled to a 150 W Ozone free Xenon lamp (6255 Oriel Instruments). The light from the UV lamp was filtered using a water filter (61945 Oriel Instruments) and then carried to the spectrophotometer holder at the right angle to the monitoring beam using an optical fiber system (77654 Oriel Instruments). 40 W m^{-2} light flux was used (Goldilux Photometer with UV-A probe). A Peltier temperature controlled (20 ºC) stirred 10 mm quartz cell (3.5 mL sample solution) was used. In a preliminary experiment, the UV-Vis absorption spectra of the closed and open forms and the λ_{max} of the open form were determined. In a second experiment the absorbance at photostationary equilibrium, A_{eq}, was measured at λ_{max} and then the decrease in the absorbance vs time was monitored.

*4.6. Photochemical behaviour of compounds **3a-b** followed by NMR spectroscopy.*

In a 5 mm NMR tube, 1.5 mg of the naphthofurans **3a-b** were dissolved in 100 μl of THF-d_8 and 400 μL of methanol-d_4 and TFA vapor was added. The amount of TFA was not quantified.

NMR spectra were recorded on Avance 500 spectrometer (^{1}H, 500 MHz) equipped with TXI probe. Photoirradiation was carried out directly into the NMR tube in a home-built apparatus with a 1000 W high-pressure Hg-Xe lamp equipped with an interferential filter at 365 nm.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at

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Highlights:

New photochromic vinylidene-naphthofurans were easily synthesised from 2-naphthol.

The naphthofurans show acidochromic properties and photochromic behaviour in acidified methanolic solutions and when adsorbed in silica gel.

This photochromic system works at room temperature switching between the uncoloured and violet state.

A mechanism for their photochromic behaviour is proposed based on NMR analysis.