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Grey colouring thermally reversible photochromic 1-vinylidene-naphthofurans

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ABSTRACT

A set of new 1-vinylidene-naphthofurans substituted by styryl groups were synthetized. These compounds show photochromic properties when adsorbed in silica gel, or in acidified THF solutions, developing intense colours after exposure to the UV light and returning to the uncoloured state, in the dark, in several minutes. The introduction of the styryl chain extends the conjugation of the photoproducts and shifts their absorption bathochromically relative to the parent unsubstituted naphthofuran. For styryl-naphthofuran **5a**, in an acidified THF solution, an intense grey colouration can be achieved after 1 min of UV exposure (or direct sunlight) and the decolouration, in the dark, occurs in less than 10 min at room temperature.

1. Introduction

While classic dyes exhibit a permanent colour, photochromic dyes have the ability to change their colouration through a reversible, light induced, isomerization reaction [1]. Usually, these smart molecules are uncoloured in the dark but are converted into a coloured photoisomer upon exposure to the UV light, which reverts back to the initial state, spontaneously or through irradiation with visible light. The photochemical reactions behind this phenomena commonly involve unimolecular reactions like *cis-trans* isomerization [2], electrocyclic ring opening/closing [3], heterolytic bond breaking [4], proton transfer [5] and induces a significant molecular modification, that changes not only the colour, but also the molecular volume [6], polarity [7], reactivity [8], solubility [9], etc. These photoswitchable properties have been explored in different ways in materials chemistry [10] and recently in some biological applications [11].

Thermally reversible photochromic molecules, like the naphthopyrans, spiropyrans and spiroxazines are photochemically converted into a thermally unstable coloured specie that returns spontaneously to the initial state, once the system is placed in the dark [1]. This phenomenon occurs typically in solution or when the molecules are dispersed in polymeric matrices, although their properties, in particular the switching speed, are particularly affected by the chemical environment surrounding the photosensitive molecule [12]. The possibility to reversibly change the colour of a lightweight material using only the sunlight attracted the industry attention that explored their application in lenses [13], windows [14] and textiles [15]. By far, the most developed technology, using these smart dyes, are the photochromic ophthalmic lens that darken under sunlight exposure. However, although a vast number of photochromic dyes have been reported and patented, few have been commercialized due to the long list of requirements that the development of a marketable product imposes [16]. The photoactive molecule must be easy and economical to synthesize, soluble in the media, uncoloured in the dark, exhibit a fast colouration under sunlight, provide an intense colouration with the require shade (grey or brown) using a low concentration of the dye, exhibit a high fading rate while not compromising a high concentration of the coloured species since these aspects tend to be mutually exclusive, show a low dependence with temperature and resist to photodegradation allowing to execute many colouration/decolouration cycles without losing their performance. Some naphthopyrans meet almost all of these requirements, but in order to reach intense colourations the industry uses compounds that

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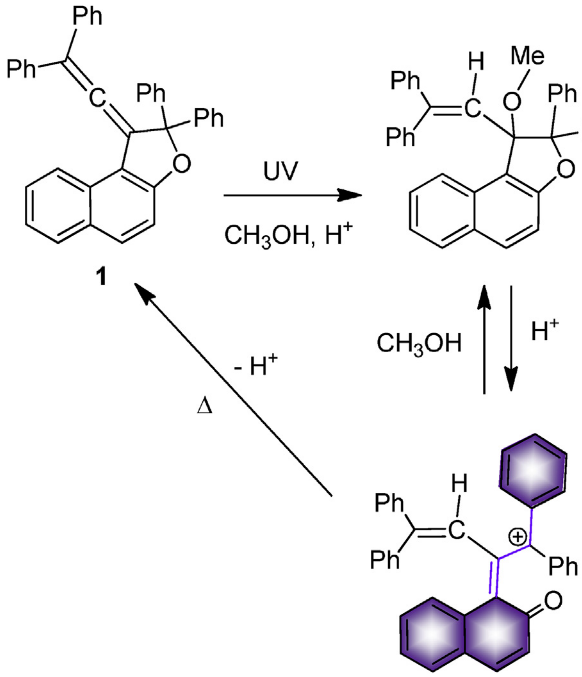
generate undesirable long-lived coloured photoisomers. In fact, although the commercial photochromic lenses are quickly activated by sunlight (<30 s), they exhibit a slow fading colour in the dark (usually more than 5 min), and thus, once the wearer goes indoors, the lenses stay coloured for too long. A fast switching system able to achieve intense grey colourations is thus actively sought by the lens industry.

We have recently discovered that 1-vinylidene-naphthofurans exhibit curious and interesting photochromic properties. These uncoloured compounds, which can be easily synthetized, are activated by UV or sunlight, affording violet coloured species that return spontaneously to the uncoloured state, in the dark, in few minutes [17]. However, while most photochromic molecules show these properties in common organic solvents, 1-vinylidene-naphthofurans require an acidic medium, such as acidified methanolic solutions, to generate the coloured species. Furthermore, they also show photochromic properties when adsorbed in silica gel. The mechanism of the reaction behind this phenomena has been establish by NMR analysis of acidified CD_3OD solutions [18]. Thus, in methanolic solution, the UV light promotes the addition of methanol to the allene group affording an uncoloured intermediate that in the presence of acid is converted into a cationic violet dye, which returns thermally to the initial closed naphthofuran in the dark (Scheme 1). These molecules show some aspects that make them potentially interesting for application in photochromic lenses. In particular, the fast activation under sunlight providing intense colourations that fade in few minutes, in the dark, at room temperature, and the preference for a silica environment which is an advantage since most coatings are based on a siloxane network.

Although hundreds of thermally reversible photochromic compounds have been studied, only a few of them are able to generate a grey colouration, which is characterized by a constant absorption throughout the visible spectra [19,20]. Therefore to generate a grey colour the industry used mainly mixtures of photochromic compounds able to generate complementary colours, but these must exhibit similar colouration and fading kinetics, otherwise during the colouration and fading a different shade is obtained which limits the range of compatible compounds. The use of a single photochromic compound allows to overcome this matching problem. Interestingly, the visible spectra of the coloured species of 1-vinylidene-naphthofurans shows two absorption bands around 440 and 570 nm which, theoretically, can be shifted bathochromically, by introducing a conjugated substituent, to generate coloured species with a broad absorption in the UV region. In the present study, we describe the synthesis of a series of substituted 1-vinylidene-naphthofurans, with an extended conjugation and evaluate their photochromic properties, under UV light at room temperature, when dispersed in silica gel and in acidified THF solutions.



Scheme 1. Photochromic equilibrium for 1-vinylidenenaphthofuran **1** in methanolic acidified solution.

2. Results and discussion

2.1. Synthesis and characterization

1-Vinylidene-naphtho[2,1-*b*]furans can be easily prepared by reaction of substituted naphth-1-ols with 1,1,4,4-tetraphenylbut-2-yn-1,4-diol in $CHCl_3$, in the presence of a catalytic amount of *p*-toluenesulfonic acid, at room temperature, in medium yields. To prepare a set of styryl substituted naphthofurans we started with compound **2**, presenting a hydroxymethyl group at carbon 7, which can be prepared in two steps from the commercially available ethyl 6-hydroxy-2-naphthoate [18]. This compound was then oxidized with PCC affording the aldehyde **3** in good yield (69%). The Wittig reaction of this aldehyde with the ylides derived from the phosphonium salts **4a-f** afforded the 7-styryl-1-vinylidene-naphthofurans **5a-f,** as a mixture of *E-Z* isomers, in medium yield (34–89%), without any perturbation of the dihydrofuran cycle (Scheme 2).

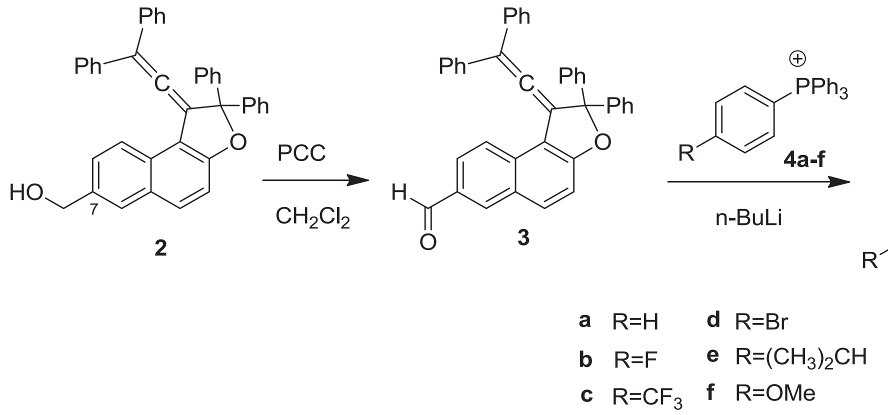
Besides the extended aromatic signals in the ^1H NMR spectrum, these compounds show two distinctive signals in the ^{13}C NMR spectrum: a low field signal around 202 ppm, characteristic of the allene function, and a signal at 95 ppm assigned to the dihydrofuran sp^3 carbon atom.

2.2. Photochromic properties in silica gel

The 1-vinylidene-naphtho[2,1-*b*]furans **1, 2, 5a-f** do not exhibit photochromic properties when exposed to the sunlight or irradiated with UV light (254 or 365 nm), in solution or in the solid state. Nevertheless, they exhibit important photochromic properties when adsorbed in acidic silica gel, a white powder with a strong absorption below 300 nm. The dispersion of the compounds **1, 2** and **5b** in the silica gel affords a white solid, while with compounds **5a, 5c-f** a slightly yellowish powder was obtained. The UV–Vis absorption spectra of the doped silica gel samples, before and after UV irradiation, was determined using a UV–Vis spectrometer equipped with an external diffuse reflectance accessory. Compounds **1** and **2** were included in this study for comparison purposes [17,18].

A sample of silica doped with naphthofuran **2,** substituted by a hydroxymethyl group, is white with a very strong absorption in the UV region below 390 nm. After UV irradiation for 1 min using a 6 W UV lamp (365 nm), this sample develops a violet colouration, characterized by two absorption maxima in the visible region at 442 and 565 nm, the latter being stronger (Fig. 1, Table 1). The unsubstituted naphthofuran **1** exhibits a similar behavior, while the compound **3,** with a carbaldehyde group, is yellow in $CHCl_3$ solution and doesn't show photochromic properties, at room temperature, when dispersed in silica.

The silica gel doped with naphthofurans **5a-f** present a very strong absorption in the UV region which extends to near 410 nm



Scheme 2. Synthesis of the 7-styryl-1-vinylidene-naphthofurans **5a-f**.

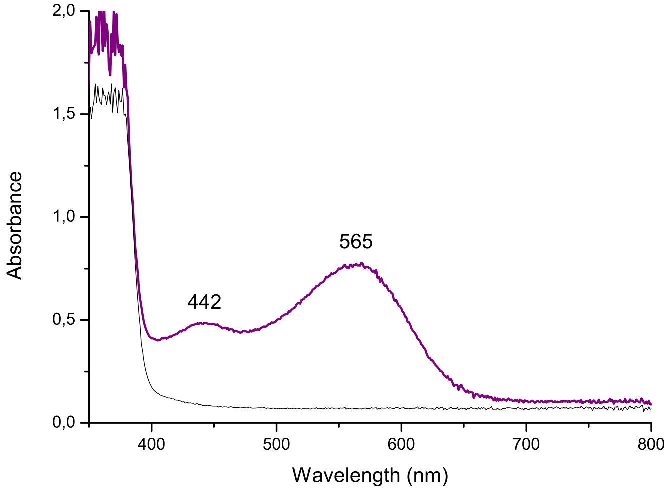


Fig. 1. Absorption spectra of silica gel doped with 1-vinylidene-naphthofuran **2** before (**black**) and after (**violet**) exposure to a 6 W UV lamp (365 nm) for 1 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

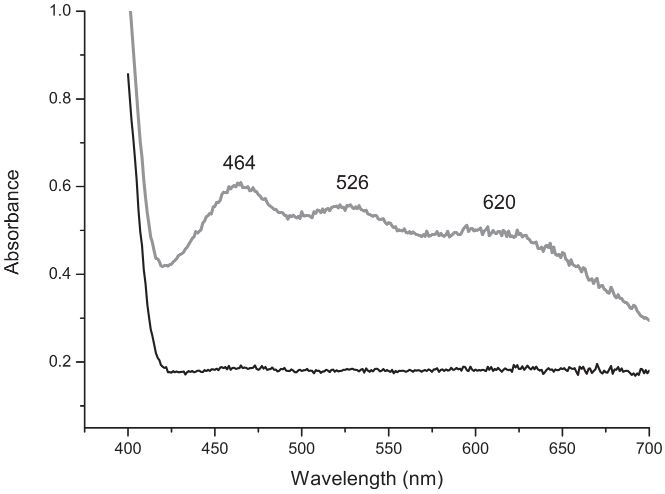


Fig. 2. Absorption spectra of silica gel doped with 1-vinylidene-naphthofuran **5a** before (**black**) and after (**grey**) exposure to a 6 W UV lamp (365 nm) for 60 s.

and therefore the samples doped with these compounds are slightly yellowish. After exposure to the UV light (6 W, 365 nm, 60 s) a broad absorption in the visible spectra that extends from 400 to 700 nm (Fig. 2) can be observed with 3 maxima of similar intensity around 460, 530 and 630 nm (the colouration is quite fast but to assure a maximal absorption, 60 s of exposure was used). This extended and homogeneous absorption confers to the samples, after irradiation, a neutral brown/grey colouration (Fig. 3, video 1). In particular, the compounds **5a-e** develop grey colours while the 8-methoxystyryl **5f** derivative affords a brownish colour (Table 1). The same colourations were observed when the samples were exposed directly to the sunlight.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.02.027.

The colouration is due to the formation of a cationic species after proton addition of the media to the alene function. This dye has an extended conjugation but the two phenyl groups of the allene and one phenyl attached to the carbocation are not in conjugation being out of the plane. This species is thermally unstable returning back to the initial closed compound in the dark (Scheme 3).

After removal of the light source, the samples lose slowly their

Table 1
Absorption maxima of silica gel doped with compounds **1**, **2**, **5a-f** after UV exposure (60 s), bleaching rate constants, half-life times and $t_{3/4}$.

Naphthofuran		λ_{max} (nm) (coloured form)	Colour	$K_{1\Delta}$ (min^{-1})	$K_{2\Delta}$ (min^{-1})	$t_{1/2}$ (min)	$t_{3/4}$ (min)
N	R						
1		442, 556	Violet	0.84 (59%)	0.20 (41%)	1.9	4.8
2		442, 565	Violet	0.68 (42%)	0.19 (0.58)	1.9	4.5
5a	H	464, 526, 620	Grey	0.15 (41%)	0.028 (59%)	12	29
5b	F	457, 523, 590	Grey	0.21 (61%)	0.036 (39%)	5.7	16
5c	CF_3	457, 526, 593	Grey	0.24 (54%)	0.043 (46%)	5.4	15
5d	Br	461, 530, 611	Grey	0.19 (54%)	0.033 (46%)	7.4	20
5e	$CH(CH_3)_2$	467, 531, 636	Grey	0.17 (45%)	0.033 (55%)	6.9	19
5f	OMe	468, 540, 650	Brown	0.16 (33%)	0.028 (67%)	13	33

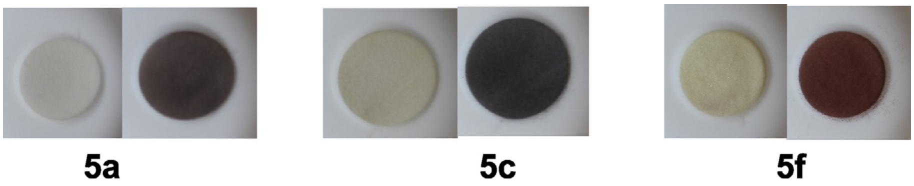
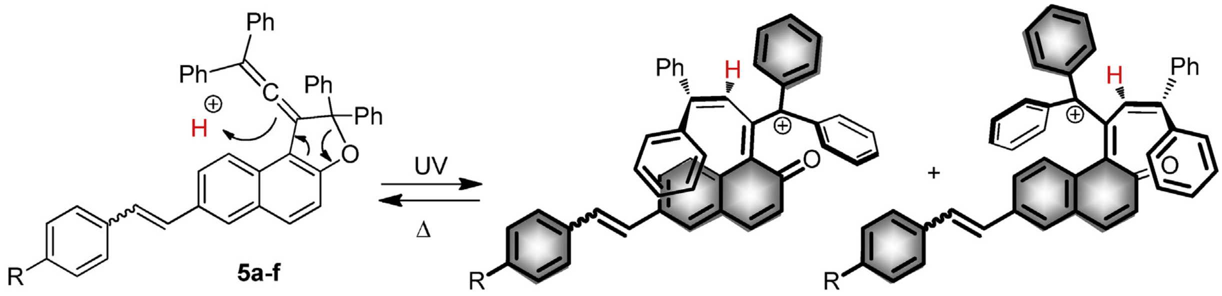


Fig. 3. Photographs of silica gel doped with compounds **5a, 5c, 5f** before and after UV irradiation (6 W, 365 nm) for 60 s.



Scheme 3. Photochromic equilibrium for 7-styryl-1-vinylidenenaphthofurans **5a-f**.

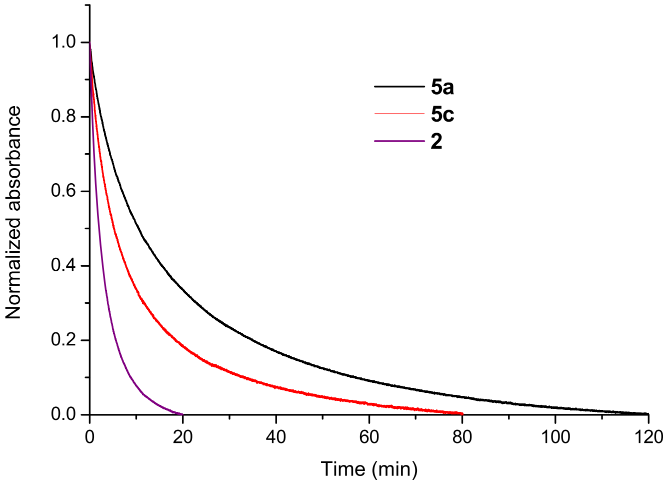


Fig. 4. Normalized thermal fading kinetics of silica gel doped with compounds **2** (violet), **5a** (black) and **5c** (red), in the dark, measured at 540 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

colouration returning to the uncoloured state in the dark. The fading kinetics of all samples was determined by recording the absorbance at 540 nm and was fitted to a bi-exponential decay equation with two rate constants of similar amplitude. All compounds show a similar behavior with the highest rate constant being responsible for the initial fast colour decay and the slowest rate constant (4–5 times lower) accountable for the small persistence of colouration that is observed. The fitting with two kinetic rates may indicate the existence of several chemical environments or two different coloured species. In fact, the overture of the dihydrofuran ring may generate two species which differ on the configuration around the double bond (Scheme 3) and should exhibit different thermal stability due to steric reasons.

Compounds **1** and **2** develop violet colourations which quickly fade away in the dark. The half-life time of the photoisomers are lower than 2 min and after 5 min the samples lose more than ¾ of the colouration. 7-Styryl-1-vinylidenenaphthofurans **5a-f** show a much slower colour decay than the hydroxymethyl substituted naphthofuran **2** as can be observed with the normalized decay kinetics (Fig. 4). After 20 min in the dark, naphthofuran **2** has returned completely to the uncoloured state while the styrylnaphthofuran **5a** takes 120 min to return to the initial state. Nevertheless, after 30 min in the dark, the small residual absorption still present in the samples is practically imperceptible to the naked eye. The compounds substituted by electron withdrawing groups (**5a,c**) show clearly a faster colour decay than the unsubstituted naphthofuran **5a,** which is in accordance with the cationic character of the coloured opened form.

The colouration process is reversible and can be repeated 10 times without significant degradation of the compounds. However, extended exposure to the UV light leads to the degradation of the compounds, confirmed by the yellowing of the samples.

2.3. *Photochromic properties in acidic solutions*

The photoswitching properties of naphthofurans are associated with the acidity of the media in which they are dispersed. In the absence of acid the compounds don't exhibit photochromic behavior while the addition of a strong acid like trifluoroacetic acid leads to the immediate formation of the coloured species (acidochromism) [17]. We have recently discovered that the addition of a small amount of sulfuric acid to methanolic/THF solutions of naphthofurans allows the observation of the photochromic phenomena in solution, however, the lifetime of the coloured species is too high, leading to a very slow decolouration process [18]. Furthermore, NMR results showed that the UV light promotes the addition of methanol to the molecules leading to the formation of a set of uncoloured side products. We have now found that there is no need to have methanol in the system and that the use of weaker acids, like acetic or formic acids, provide much more interesting results.

The naphthofurans **5a-f** show low solubility in acetic or formic acid but they are very soluble in THF. Thus, several solutions of naphthofuran **5a** in THF/HOAc and THF/HCOOH were prepared and tested for their photochromic activity. The initial solutions are nearly uncoloured but after irradiation with a high power laser (200 mW, 405 nm), for 1 min, they become coloured exhibiting a wide absorption in the visible region with 3 maxima of similar

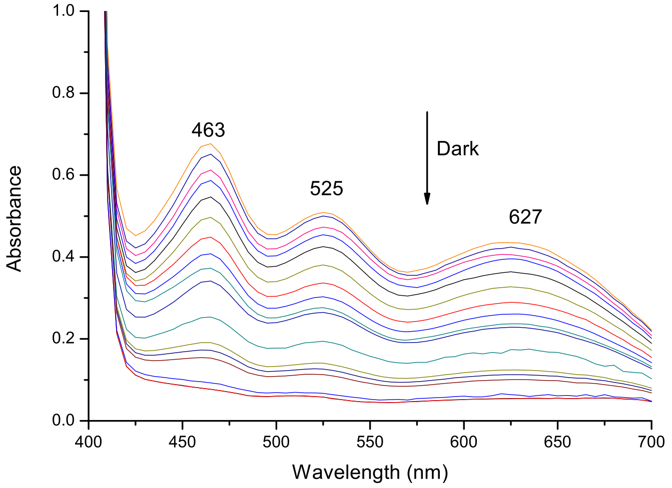


Fig. 5. Time evolution of the visible spectra of naphthofuran **5a** in THF/HCOOH (2/0.5) during thermal fading after UV activation with a high power laser (200 mW, 405 nm) for 60 s.

intensity, which can be described as grey (Fig. 5, video 2).

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.02.027.

Then, when the light is removed the colouration decreases following a biexponential kinetic model. Under steady state conditions the maxima absorption is inversely related to the bleaching kinetics and thus higher intensities are attained with slower systems. The interconversion between the two isomers can be performed in THF/HOAc (0.5/2) but it requires an excessive amount of acid which limits the solubility of the naphthofuran. The best results were obtained dissolving the naphthofuran **5a** in a mixture of THF/HCOOH but the amount of formic acid is very important: a low concentration originates a very low concentration of the coloured species and a fast discolouration kinetic, while an excess of acid leads to a very slow fading. A good balance between these two aspects was obtained in THF/HCOOH (2:0.5) with a maximum absorbance of 0.68 (Table 2). This solution is grey after UV irradiation and loses half of the colouration in 2.36 min and its $t_{3/4}$ is 5.19 min. The sample returns completely to the initial state in 20 min, but after 10 min the residual colour is no longer perceptible to the naked eye. A lower amount of formic acid leads to a faster switching but at the same time to a lower absorbance.

The detection of two fading kinetics in solution is an indication that most likely two very similar coloured species are formed after UV activation. The addition of one proton to the allene and overture of the dihydrofuran ring leads to the formation of a chemical species which, considering its cationic nature, may suffer a rotation of the double bond affording a second diastereoisomeric dye (Scheme 3). These species should established a fast equilibrium due to their cationic nature, but exhibit different thermal stability due to steric reasons. The species with the carbocation on the same side of the carbonyl should be less thermally stable and fade more quickly.

Fig. 6. Photographs of THF/HCOOH solutions of compounds **5a** and **5f** before and after UV irradiation (laser 200 mW, 405 nm).

Under the same conditions naphthofurans **1, 2, 5b, 5e** provide uncoloured solutions while solutions of compounds **5c,d** and **5f** are slightly yellow. UV irradiation with a UV laser (200 mW, 405 nm) for 60 s gave grey/green/brown solutions which returned to the initial state in the dark after several minutes (Fig. 6).

Naphthofurans **1, 2,** which exhibited a fast switching in silica gel, displayed a very slow response in this acid solution. The absorbance after 1 min of irradiation is too low (0.12–0.33) and the lifetime of the violet coloured species is too high leading to a slow switching between the coloured and uncoloured species.

The styryl-vinylidene-naphthofurans **5a-f** show a better behavior with higher absorbances and faster kinetics. Compound **5a** exhibited a grey colouration after UV irradiation and an half-life time of 2.36 min. The introduction of a CF_3 group or a bromine atom in the *para* position intensified the initial yellowish colouration and after UV irradiation a green/grey colouration was observed. At the same time an increase of the fading kinetics was observed: while the complete discolouration of compound **5a** takes around 10 min, compound **5c**, with a CF_3 substituent, returns to the initial yellowish state in less than 5 min. The introduction of a methoxy group (compound **5f**) changed the colour of the photoisomer from grey to brown and increased its thermal stability and thus for this compound the fading process is considerable slower as can be observed in the normalized Fig. 7. After UV irradiation the solution of compound **5b**, with a fluorine atom, becomes green and the coloured photoisomer exhibits a surprising high thermal stability and thus a slow thermal decay. This behavior may be due to the establishment of hydrogen bonds with the formic acid.

This system has a reproducible behavior and several UV exposure/dark cycles can be performed, however, as observed with the compounds in silica gel, the extended exposure to the UV light leads to the progressive degradation of the compounds confirmed by the yellowing of the samples and the lowering of the maximal absorbance at 540 nm (Fig. 8). To prevent this side reaction it will be important to understand the nature of these photoproducts.

The behavior of these compounds in silica gel and in acidified solution indicates that the naphthofurans can switch between the

Table 2
Absorption maxima of compounds **1, 2, 5a-f** in THF/HCOOH (2/0.5) after UV exposure, bleaching rate constants, half-life times and $t_{3/4}$.

Naphthofuran	λ_{max} (nm) (coloured form)	A_{max}	Colour	$K_{1\Delta}$ (min^{-1})	$K_{2\Delta}$ (min^{-1})	$t_{1/2}$ (min)	$t_{3/4}$ (min)
1	443, 575	0.12	Violet	0.080 (57%)	0.029 (43%)	11.0	22.6
2	445, 575	0.33	Violet	0.096 (17%)	0.037 (83%)	13.7	26.8
5a	463, 525, 627	0.68	Grey	0.60 (35%)	0.19 (65%)	2.36	5.19
5b	460, 520, 610	1.02	Green	0.065 (50%)	0.019 (50%)	15.9	33.56
5c	458, 520, 615	0.47	Grey	1.13 (59%)	0.68 (41%)	0.76	1.53
5d	463, 524, 623	0.65	Grey	0.82 (23%)	0.36 (77%)	1.54	3.27
5e	467, 530, 638	0.94	Grey	0.16 (30%)	0.042 (70%)	9.64	21.02
5f	470, 535, 668	1.00	Brown	0.27 (36%)	0.06 (64%)	6.61	15.78

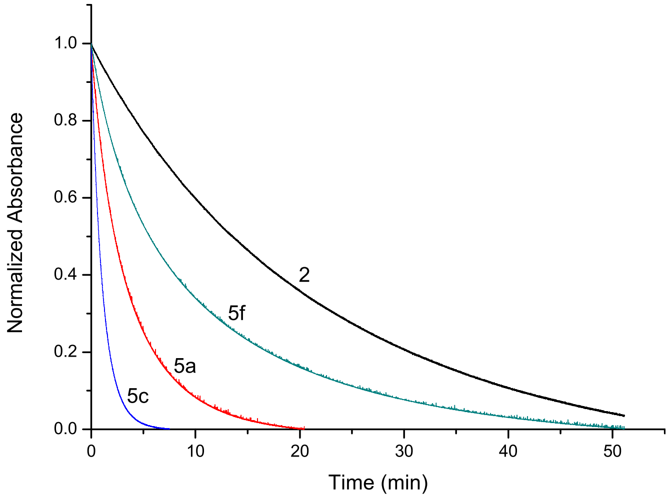


Fig. 7. Normalized thermal fading kinetics of compounds **2 5a, 5c, 5f** in THF/HCOOH, in the dark, measured at 540 nm.

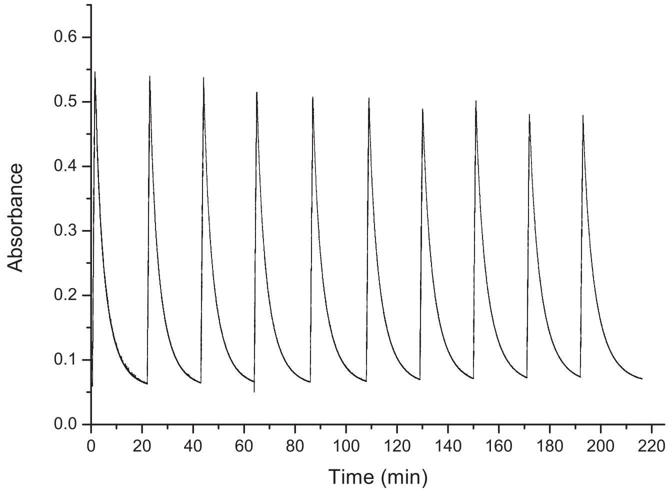


Fig. 8. UV exposure (60 s)/dark cycles of naphthofuran **5a** in THF/HCOOH at 20 °C.

uncoloured and grey colourations in different chemical environment depending on their acidity. The need to have an acidic media to observe photochromism with these compounds is not a limitation for their application as photochromic coatings since many organic-inorganic hybrid matrices are compatible with an acidic media.

3. Conclusion

The introduction of a styryl chain in the structure of the vinylidene-naphthofurans leads to a new set of uncoloured photochromic compounds that afford grey/brown colourations upon exposure to the UV or sunlight, at room temperature. The photochromic properties of these smart dyes are very sensitive to the chemical environment, specially their acidity being faster in THF/HCOOH solution than in silica gel. The amount of formic acid influences the kinetics of the fading reaction as a low concentration leads to a faster system but with a lower colourability. A good compromise was obtained in THF/HCOOH (2/0.5) solutions. The substituents in the styryl group influences the kinetic of the fading process: Electron-withdrawing groups like Br or CF_3 increases the fading rate leading to fast switching compounds but confers an initial yellowish colour to the solution before irradiation. For compound **5a** an intense grey colouration (Abs = 0.47)) was achieved after 60 s of UV exposure and the system returned spontaneously to the uncoloured state, in the dark, in less than 10 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 ^{1}H NMR spectroscopy. IR spectra were obtained on a Shimadzu IRAffinity spectrometer using an ATR module. Wavenumbers 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 determined with a VG AutoSpec M spectrometer. Melting points were determined using a microscope URAC with an heating plate and are uncorrected. High purity grade silica gel 60 (63–200 µm) µm was used. 1,1,4,4-Tetraphenylbut-2-yn-1,4-diol and 1-vinylidene-naphthofurans **1** and **2** were prepared using published methods [17,18]. The phosphonium salts **4a-f** were prepared using standard procedures [21].

4.2. Synthesis

1-(2,2-diphenylvinylidene)-2,2-diphenyl-1,2-dihydronaphtho[2,1-*b*]furan-7-carbaldehyde **3.** Pyridinium chlorochromate (0.610 g, 2.84 mmol, 1.5 eq) was added to a solution of naphthofuran **2** (1.0 g, 1.89 mmol) in CH_2Cl_2 (50 mL) and the suspension stirred overnight at room temperature. The brown suspension was filtered over Celite and the solid washed with Diethyl ether (3 × 20 mL). The filtrate was evaporated and the crude product purified by column chromatography (20% Ethyl acetate/Petroleum ether). The compound was recrystallized from Ethyl acetate/Petroleum ether and obtained as yellowish crystals (0.689 g, 69%). **Mp** 230.6–233.8 °C. **IR** (cm^{-1}): 3060, 2826, 1707, 1687, 1618, 1466, 1280, 1231, 1148, 956, 824, 748, 686, 638. **^{1}H NMR** (400 MHz, $CDCl_3$): 10.07 (s, 1H), 8.3 (m, 2H), 7.9 (m, 2H), 7.42 (m, 4H), 7.35 (d, 1H, J = 8.8 Hz), 7.3–7.2 (m, 12H), 7.10 (m, 4H). **^{13}C NMR** (100 MHz,$CDCl_3$): 202.6, 191.8, 160.1, 142.5, 136.0, 134.9, 133.4, 133.1, 132.0, 130.0, 128.6, 128.4, 128.2, 128.1, 127.9, 127.7, 125.3, 123,0, 117.9, 114.4, 113.8, 113.6, 95.5. **EI-MS (TOF)** *m*/*z* (%): 526 (100), 449 (63), 421 (22), 359 (30), 313 (28), 277 (85), 258 (62), 181 (99), 167 (54). **HRMS** calcd for $C_{39}H_{26}O_2$: 526.1935. Found: 526.1933.

4.2.1. Synthesis of naphthofurans 5a-f. General procedure

n-BuLi (0.32 mL, 1.6 M in hexanes, 1.5 eq) was added to a cold (0 °C) solution of triarylphosphonium salt **4a-f** (0.51 mmol, 1.5 eq) in dry THF (15 mL). The yellow solution was left at room temperature for 30 min and then a solution of naphthofuran **3** (180 mg, 0.342 mmol) in dry THF was added. After 2 h at room temperature the THF was evaporated, water was added (30 mL) and the solution was extracted with AcOEt (5 × 20 mL). The organic phase was washed with water (2 × 20 mL), dried and evaporated to afford the crude naphthofuran **5a-f** that was purified by column chromatography (10% Ethyl acetate/Petroleum ether) or recrystallized from CH_2Cl_2/petroleum ether.

*4.2.1.1. 1-(2,2-diphenylvinylidene)-2,2-diphenyl-7-styryl-1,2-dihydronaphtho[2,1-b]furan **5a**.* 94 mg (Yellowish crystals), 46% yield. **IR** (cm^{-1}): 3039, 1597, 1494, 1445, 1255, 1031, 956, 817, 741, 693, 645. **^{1}H NMR** (400 MHz, CDCl$_3$): 8.27 (d, J = 8.6 Hz, 0.7 H), 8.10 (d, J = 8.7 Hz, 0.3 H), 8.0–7.0 (m, 30 H), 6.71 (d, J = 12.2 Hz, 1H), 6.65 (d, J = 12.1 Hz, 1H). **^{13}C NMR** (100 MHz,CDCl$_3$); two isomers: 202.8, 202.7, 1257.9, 142.9, 137.4, 137.2, 136.4, 132.7, 132.6, 131.8, 130.3, 130.1, 130.0, 129.9, 129.2, 129.1, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.7, 127.5, 127.3, 127.1, 126.4, 128.4, 122.6, 121.9, 117.3, 114.7, 114.6, 113.8, 113.6, 112.5, 94.9. **EI-MS (TOF)** m/z (%): 600 (100), 523 (62), 433 (73). **HRMS** calcd for C$_{46}$H$_{32}$O$_2$: 600.2457. Found: 600.2453.

4.2.1.2. 1-(2,2-diphenylvinylidene)-7-(4-fluorostyryl)-2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan ***5b***. 76 mg (slighty yellow crystals), 36% yield. **IR** (cm^{-1}): 3046, 1611, 1500, 1452, 1328, 1259, 1162, 1107, 1058, 942, 824, 769, 686, 631. **^{1}H NMR** (400 MHz, CDCl$_3$): 8.2 (d, 1H, J = 8.2 Hz), 7.8–7.7 (m, 3H), 7.4 (m, 6H), 7.3–7.0 (m, 21 H). **^{13}C NMR** (100 MHz,CDCl$_3$): 202.8, 163.5, 161.0, 158.0, 142.9, 136.4, 133.60, 133.57, 132.55, 131.81, 130.27, 129.24, 128.7, 128.4, 128.1, 127.9, 127.83, 127.75, 127.65, 127.28, 127.1, 125.4, 122.6, 117.4, 115.7, 115.5, 114.6, 113.8, 112.8, 95.0. **ESI-MS** m/z (%): 619 (M + H, 100), 421 (45), 403 (60). **HRMS** calcd for C$_{46}$H$_{31}$FO: 618.23615. Found: 618.23535.

4.2.1.3. 1-(2,2-diphenylvinylidene)-2,2-diphenyl-7-(4-(trifluoromethyl)styryl)-1,2-dihydronaphtho[2,1-b]furan ***5c***. 203 mg (yellow crystals), 89% yield. **IR** (cm^{-1}): 3046, 2342, 2307, 1584, 1500, 1438, 1321, 1273, 1162, 1121, 1065, 942, 831, 762, 693. **^{1}H NMR** (400 MHz, CDCl$_3$): 8.26 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.6 Hz, 1H), 7.78 (s, 1H), 7.75–7.5 (m, 8H), 7.5–7.0 (m, 18H), 6.80 (d, J = 12 Hz, 1H), 6.61 (d, J = 12 Hz, 1H). **^{13}C NMR** (100 MHz,CDCl$_3$); two isomers: 202.8, 202.6, 158.1, 142.9, 140.9, 136.3, 132.1, 132.0, 131.8, 131.1, 130.2, 123.0, 129.6, 129.2, 129.0, 128.7, 128.42, 128.37, 128.2, 127.9, 127.8, 127.3, 126.7, 126.5, 125.6, 125.4, 125.1, 122.7, 122.1, 117.5, 117.4, 114.6, 114.0, 113.7, 113.0, 112.7, 95.0. **ESI-MS** m/z (%): 669 (M + H, 100), 557 (59), 421 (37), 282 (37). **HRMS** calcd for (M+1): C$_{47}$H$_{32}$F$_3$O: 669.23998. Found: 669.24010.

4.2.1.4. 1-(2,2-diphenylvinylidene)-2,2-diphenyl-7-(4-bromostyryl)-1,2-dihydronaphtho[2,1-b]furan ***5d***. 133 mg (yellow crystals), 58% yield. **IR** (cm^{-1}): 3039, 2314, 1597, 1487, 1438, 1252, 1231, 1072, 99, 796, 769, 693, 624. **^{1}H NMR** (400 MHz, CDCl$_3$): 8.29 (d, 1H, J = 8.7 Hz), 8.14 (d, J = 8.7 Hz, 1.2H), 7.9–7.0 (m, 27H), 6.76 (d, J = 12.2 Hz, 1H), 6.56 (d, J = 12.2 Hz, 1H). **^{13}C NMR** (100 MHz,CDCl$_3$); two isomers: 202.8, 202.6, 158.1, 142,9, 136.4, 136.0, 132.4, 132.3, 131.1, 131.9, 131.8, 131.4, 130.7, 130.6, 130.3, 130.0, 129.4, 129.3, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.3, 127.0, 125.3, 122.6, 122.0, 121.2, 121.0, 117.4, 114.6, 113.9, 113.6, 112.9, 112.6, 94.97, 94.93. **ESI-MS** m/z (%): 680 (M^{+}+2, 97), 678 (M^{+}, 100), 603 (56), 601 (59), 513 (90), 511 (84), 413 (16), 313 (23). **HRMS** calcd for C$_{46}$H$_{31}$BrO: 678.1558. Found: 678.1576.

4.2.1.5. 1-(2,2-diphenylvinylidene)-7-(4-isopropylstyryl)-2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan ***5e***. 146 mg (yellow crystals), 67% yield. **IR** (cm^{-1}): 3046, 2956, 1597, 1494, 1445, 1273, 1031, 956, 824, 762, 693, 652. **^{1}H NMR** (400 MHz, CDCl$_3$); two isomers: 8.26 (d, J = 8.7 Hz, 1H), 8.10 (d, J = 8.6 Hz, 1H), 7.9–7.8 (m, 4H), 7.68 (d, J = 8.9 Hz, 1H), 7.6–7.0 (m, 47 H), 6.68 (d, J = 12.2 Hz, 0.7H), 6.62 (d, J = 12.2 Hz, 0.7H), 3.0–2.8 (m, 1.7H, CH), 1.30 (d, J = 6.7 Hz, 6H), 1.23 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz,CDCl$_3$); two isomers: 202.8, 202.7, 157.9, 148.5, 147.9, 142.9, 136.4, 135.0, 134.6, 132.9, 131.8, 130.3, 130.2, 130.1, 129.3, 129.1, 129.0, 128.9, 128.4, 128.3, 127.1, 127.9, 127.7, 127.5, 127.3, 126.8, 126.4, 126.2, 125.5, 122.5, 121.8, 117.4, 117.3, 114.7, 114.6, 113.8, 113.6, 112.7, 112.4, 94.89, 94.85, 33.89, 33.80, 23.92, 23.87. **ESI-MS** m/z (%): 643 (M + H, 100), 421 (8), 403 (10), 393 (14), 265 (8), 249 (10). **HRMS** calcd for C$_{49}$H$_{38}$O: 642.2917. Found: 642.2921.

4.2.1.6. 1-(2,2-diphenylvinylidene)-2,2-diphenyl-7-(4-methoxystyryl)-1,2-dihydronaphtho[2,1-b]furan ***5f***. 181 mg (yellow crystals), 84% yield. **IR** (cm^{-1}): 3052, 1584, 1514, 1466, 1245, 1176, 1024, 942, 824, 762, 686, 617, 514. **^{1}H NMR** (400 MHz, CDCl$_3$); two isomers: 8.26 (d, J = 8.7 Hz, 1H), 8.12 (d, J = 8.6 Hz, 0.5H), 7.9–6.9 (m, 43H), 6.76 (d, J = 8.5 Hz, 1H), 6.63 (d, J = 12.1 Hz, 1H), 6.58 (d, J = 12.2 Hz, 1H), 3.86 (s, 3H, OMe), 3.79 (s, 0.6H, OMe). **^{13}C NMR** (100 MHz,CDCl$_3$); two isomers: 202.8, 202.7, 159.2, 159.0, 158.7, 157.9, 157.8, 142.9, 136.4, 133.1, 133.0, 131.7, 130.5, 130.3, 130.2, 130.1, 129.7, 129.6, 129.0, 128.9, 128.8, 128.4, 128.3, 128.1, 127.9, 127.7, 127.6, 127.4, 127.3, 127.2, 126.5, 126.2, 125.4, 122.5, 121.9, 117.3, 114.7, 114.1, 114.1, 113.8, 112.7, 112.4, 94.9, 55.3, 55.1.

ESI-MS m/z (%): 630 (M^{+}, 93), 552 (57), 463 (100). **HRMS** calcd for C$_{47}$H$_{34}$O$_2$: 630.2559. Found: 630.2551.

*4.3. Photochromism of naphthofurans **1, 2, 5a-f** in silica*

4.3.1. Preparation of the doped silica gel

To a solution of naphthofurans **1, 2, 5a-f** (5.0 mg) in CH$_2$Cl$_2$ (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 overnight, in dark, until the complete evaporation of the solvent at atmospheric pressure.

4.3.2. Spectra measurements before and after UV irradiation

The samples powder were placed on a teflon support and a Vilber-Lourmat lamp (365 nm, 6 W) was positioned over the samples. The UV light was switch on for 60 s during which all samples developed a violet/grey/brown colouration. The UV–Vis spectra of the solid samples, before and after UV irradiation was recorded using a UV–Vis spectrophotometer 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 °C. The fading 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.

*4.4. Photochromism of naphthofurans **1, 2, 5a-f** in MeOH/HCOOH solution*

4.4.1. Preparation of the solution

2 mg of the naphthofurans ***1, 2, 5a-f*** were dissolved in 2.0 mL of THF and then 0.5 mL of formic acid was added. This solution was transferred into a Quartz UV–vis Cell.

4.4.2. Spectrokinetic studies under continuous irradiation

UV irradiation experiments were made using a CARY 50 Varian spectrometer equipped with a Peltier temperature module (20 °C) using a 10 mm quartz cell (2.5 mL sample solution) with continuous stirring. The solution was irradiated from the top of the cell using a high power UV laser (405 nm, 200 mW). In a preliminary experiment, the UV–Vis absorption spectra in the dark and after UV exposure were determined. In a second experiment cycles of UV irradiation/dark were performed recording the absorbance vs time at λ_{max} of the coloured species during irradiation and after the irradiation ceased. The fading 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.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.02.027.

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