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Colour switching with photochromic vinylidene-naphthofurans

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ABSTRACT

A series of novel photochromic vinylidene-naphthofurans with extended conjugation, and a free hydroxyl function, were easily prepared using the Suzuki reaction. After silanization, these dyes were embedded in ormosil matrices affording solid and transparent materials that acquire different colourations (violet, green, bluish), reversibly, when exposed to the UV (Sun) light, for 2 min, at room temperature. The presence of an extra phenyl ring in some positions affects both the λ_{max} of absorption of the photochromic compounds in the uncoloured closed and open coloured form. After removal of the light source the materials lose progressively their colouration returning to the initial uncoloured state in less than 15 min at room temperature.

1. Introduction

Photochromic colorants can change reversibly their colouration through the action of light which promotes an isomerization reaction leading to coloured species. For T-type photochromic compounds the coloured photoisomer is thermally unstable and returns spontaneously to the initial form when the light source is removed [1]. These photoactive compounds have been successfully used in the production of ophthalmic lenses that darken under sunlight. However, although many types of photochromic compounds are known, which exhibit a wide variation in behavior, only a few have been considered by the lens industry since their requirements are very specific [2]. The compounds must be uncoloured in the dark, be UV active, change quickly to grey after exposure to the sunlight, develop an intense colouration, work at room temperature, have a small dependence on temperature, return to the uncoloured state after a few minutes in the dark and resist to photodegradation over a long period of time [3]. Nowadays, the industry uses mainly complex naphthopyrans that fulfill most of the above characteristics but exhibit a rather slow fading in the dark, which means that the compounds have a slow adaptation to a changing UV light environment.

Vinylidene-naphthofurans are a new class of polycyclic compounds that exhibit photochromic properties at room temperature but, unlike common photochromic compounds, they require an acidic environment and UV light to generate the coloured species [4]. The photochromic mechanism involves the UV light promoted addition of one proton, from the environment, to the allene group with overture of the furan ring leading to a coloured carbocation with two absorption bands in the visible region (451 nm and 580 nm) (Scheme 1). In the absence of light this species returns spontaneously to the uncoloured closed form, in few minutes, at room temperature [5].

This system possess some characteristics that makes them potentially useful for industrial applications especially in ophthalmic lenses: 1) these molecules can be easily prepared from the reaction of 2-naphthols with readily available tetraarylbut-2-yne-1,4-diols at room temperature; 2) they are activated by the sunlight at room temperature; 3) develop intense colours with two absorption bands which opens the opportunity to obtain a grey colouration; 4) bleach in few minutes, at room temperature, in the dark [3].

The unsubstituted vinylidene-naphthofuran **1** (Scheme 1) exhibits a strong absorption in the UV region (λ_{max} at 373 nm) but a low absorption near 400 nm. This aspect is very relevant since the UV sunlight intensity is higher near 400 nm and the polymeric materials used usually in the production of ophthalmic lenses, CR-39, also absorb intensively in the UV region below 385 nm (the transmittance drops from 90% at 400 nm to 65% at 385 nm), which limits the absorption of light by the photoactive molecule [6]. On

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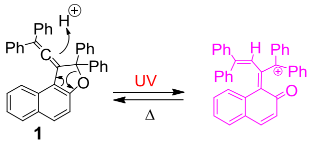


Scheme 1. Photochromic behavior of vinylidene-naphthofuran **1**.

the other hand, a significant absorption above 400 nm means that the compound has initially an yellow colouration which is undesirable. Therefore, the ideal photochromic molecule should be uncoloured, absorb intensively in the UV region just below 400 nm and develop a strong absorption in the visible region after UV or sunlight irradiation [7].

In the closed form the four phenyl groups are not co-planar with the dihydronaphthofuran ring and the compound absorbs only the UV region, but upon ring opening there is a substantial bathochromic shift indicative of the conjugation with one or more phenyl groups. Accordingly, the introduction of substituents on the phenyl groups will affect mainly the λ_{max} of the open form while the changes in the naphthalene ring may have an effect on both the closed and open forms.

The vinylidene-naphthofurans operate well in acid medium and can be embedded in ormosil matrices producing uncoloured transparent materials [8]. However, the unsubstituted vinylidene-naphthofuran **1** shows a limited solubility in these conditions leading to its precipitation during the condensation reactions of the siloxane monomers and hardening of the material. To avoid this problem it is preferable to introduce, in the molecule, a siloxane reactive group able to establish a chemical linkage with the matrix. This can be done by treatment of hydroxyl substituted compounds with (triethoxysilyl)propyl isocyanate [9]. Taking into account these considerations we designed three new vinylidene-naphthofurans possessing an extra phenyl group, in different positions, to extend the conjugation and induce a bathochromic shift in the wavelength of absorption of the uncoloured and coloured forms, and a reactive OH function necessary to introduce a reactive triethoxysilylpropyl chain. The linkage of the photoactive molecule to the matrix was performed from 3 different positions: from the naphthalene core (1), the allene group (2) and from the *sp* [3] aromatic rings (3) (Scheme 2). The photochromic behavior of the materials obtained using these photoactive molecules will allow to understand the effects of the extra conjugated aromatic ring and the point of linkage of the molecule to the matrix.

2. Results and discussion

2.1. Synthesis

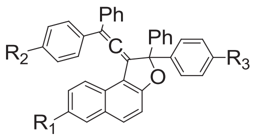
Vinylidene-naphthofurans can be easily obtained through the acid catalyzed reaction of 2-naphthols with tetraarylbut-2-yne-1,4-diols [4]. This cascade reaction occurs at room temperature and is very versatile allowing the preparation of differently substituted vinylidene-naphthofurans. The tetraarylbut-2-yne-1,4-diols can be easily obtained through the reaction of 1,1-diarylpropynols with *n*-BuLi followed by addition of arylketones. Following this approach the diols **2a-c** were prepared starting from *p*-bromobenzophenone, benzophenone *and p*-methoxybenzophenone, respectively.

The reaction of 2-naphthol with diol **2a,** catalyzed by *p*-toluenesulfonic acid at room temperature, gave compound **3a** in good yield (78%) while the reaction of 6-bromo-2-naphthol with tetraarylbut-2-yne-1,4-diols **2b,c**, afforded the bromo substituted vinylidene-naphthofurans **3b,c** (73–97%) (Scheme 3).

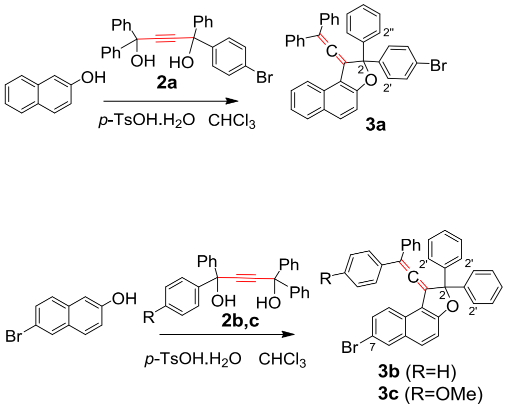
Besides the extended aromatic signals in the ^{1}H NMR spectrum, the polyaromatic compounds **3a-c** exhibit two characteristic signals in the ^{13}C NMR spectrum: a low field signal around 202 ppm, characteristic of the allene function, and a signal at 94–95 ppm assigned to the dihydrofuran *sp* [3] C-2 carbon atom. The HMBC spectrum of compound **3c** (R = OMe) showed a strong correlation between the *sp* [3] C-2 carbon at 95.0 ppm and the four protons H-2′ of the phenyl groups at 7.48 ppm, indicative that the *p*-methoxyphenyl ring is linked to the allene group. For compound **3a** the HMBC showed a strong correlation between the *sp* [3] C-2 carbon at 94.3 ppm and two sets of aromatic protons (H-2′ and H-2″) of the phenyl and *p*-bromophenyl substituents at 7.47 and 7.37 ppm, which indicates that the *p*-bromophenyl group in linked to the C-2 of the dihydrofuran ring (Scheme 3).

This one-pot reaction occurs via a domino reaction (Scheme 4): under acid-catalysis the diol **2** is converted into a propargylic carbocation, which upon reaction with 2-naphthol provides a propargylic aryl ether. Then, this intermediate performs a [3,3]-sigmatropic Claisen rearrangement followed by enolization and acid-catalyzed intramolecular dehydration affording the final vinylidene-naphthofuran **3**. The selectivity observed with diols **2a,c** is a consequence of the effect of the methoxy and bromine substituents on the stability of the initial propargylic carbocation. The electron donating methoxy group will stabilize a positive charge on carbon 1 of the diol **2c,** while with the electron withdrawing bromine atom (diol **2a**) the positive charge with be formed preferentially on carbon 4 (Scheme 4). Therefore, following the proposed mechanism, the methoxy group with appear in the allene phenyl rings (compound **3c**), while the bromine atom with end in the C-*sp* [3] phenyl rings (compound **3a**).

The Suzuki reaction of compounds **3a,b** with *p*-(hydroxymethyl) phenylboronic acid, catalyzed by tetrakis (triphenylphosphine) palladium afforded, respectively, the vinylidene-naphthofurans **5a** and **5b,** in good yield (79–84%), while the reaction of compound **3c** with phenylboronic acid gave the phenyl substituted compound **4c** (85%) which was then deprotected with BBr_3 affording the phenolic vinylidene-naphthofuran **5c** (76%) (Scheme 5).



Scheme 2. Positions of the linkage of the vinylidene-naphthofuran molecule to the matrix.



Scheme 3. Synthesis of bromo substituted vinylidene-naphthofurans **3a-c** from naphthols.

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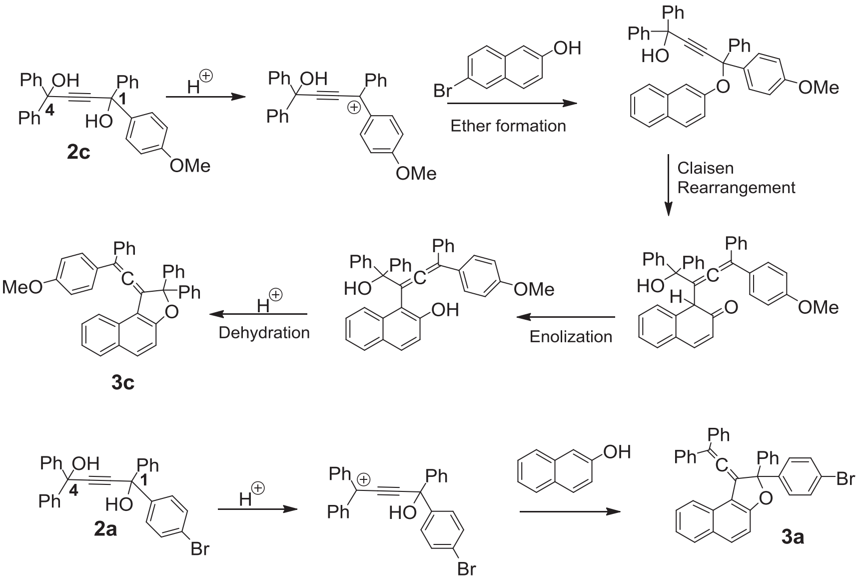
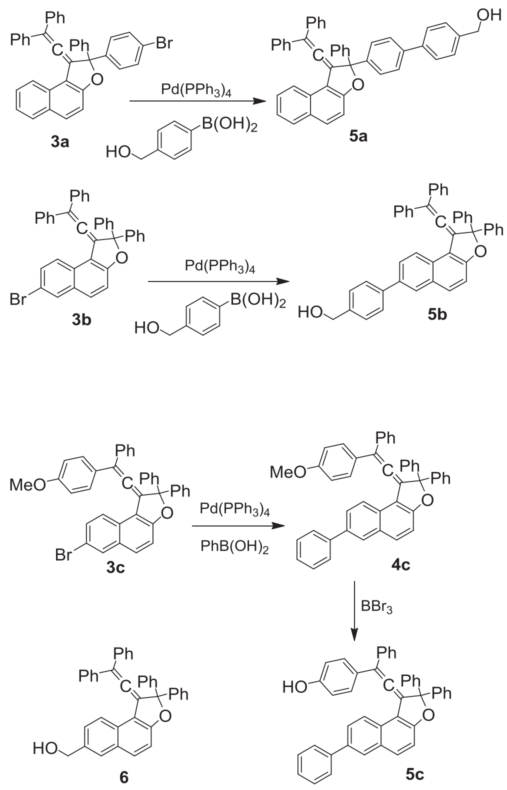


Scheme 4. Mechanism for the formation of substituted vinylidene-naphthofurans **3a,c** from tetrarylbut-2-yne-1,4-diols **2a,c**.



Scheme 5. Synthesis of the hydroxylated vinylidene-naphthofurans **5a-c** using the Suzuki reaction and the structure of the reference compound **6** [5].

2.2. UV–vis spectral analysis

Chloroform solutions of vinylidene-naphthofurans **3, 4, 5** (5.0×10^{-5} M) are uncoloured with a strong absorption in the UV region. Figs. 1–3 show the UV–vis spectra of these compounds compared with the 7-hydroxymethyl-tetraphenylvinylidene-naphthofuran **6**.

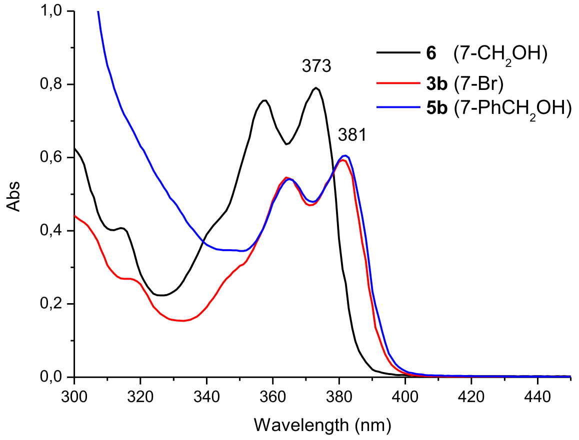


Fig. 1. UV–vis absorption spectra of vinylidene-naphthofurans **3b, 5b** and the parent compound **6** substituted by a CH_2OH group, in $CHCl_3$.

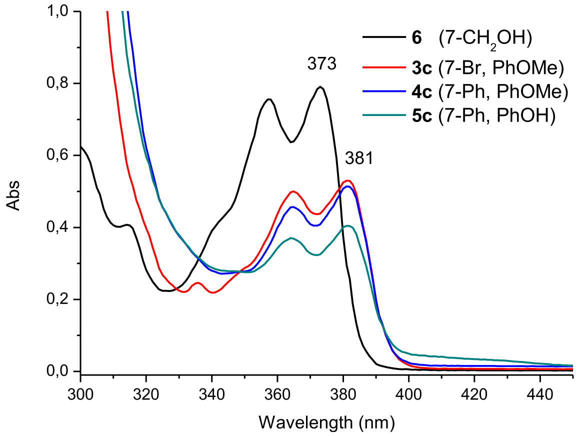


Fig. 2. UV–vis absorption spectra of vinylidene-naphthofurans **3c, 4c, 5c** and the parent compound **6** substituted by a CH_2OH group, in $CHCl_3$.

From Fig. 1 it is clear that the introduction of bromine or *p*-(hydroxymethyl)phenyl groups in the 7 of the naphthofuran ring (compounds **3b, 5b**) has a significant effect on the λ_{max} of the

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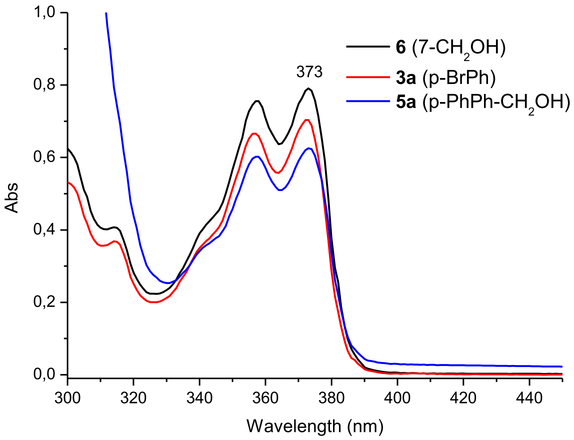

Fig. 3. UV–vis absorption spectra of vinylidene-naphthofurans **3a, 5a** and the parent compound **6** in $CHCl_3$.

compounds promoting a bathochromic shift of 8 nm. This may be rationalized based on the extension of the conjugation brought by the extra phenyl ring or bromine atom. The same effect was observed with compounds **3c, 4c, 5c**: after the introduction of a bromine or a phenyl group in the 7-position, a 8 nm bathochromic shift of the λ_{max} of the closed vinylidene-naphthofurans was observed (Fig. 2).

On the contrary, the introduction of the same groups on the *para* position C-*sp* [3] phenyl groups (compounds **3a, 5a**), as well as the deprotection of the methoxy group (compounds **4c, 5c** Fig. 2) has practically no effect on the absorption of the closed vinylidene-naphthofurans (Fig. 3). This confirms the prediction that, in the closed form, the four phenyl rings are not conjugated with the dihydronaphthalene.

Hence, compounds **5b** and **5c** absorb at higher wavelengths in the UV region than the parent compound **6,** and they possess a free hydroxyl function which allows the introduction of a reactive siloxane chain necessary to link the compounds to the matrix.

2.3. *Acidochromic properties*

Besides photochromic properties, the vinylidene-naphthofurans show also acidochromic properties. In the presence of strong acids the uncoloured vinylidene-naphthofuran **1** is converted into a stable cationic species (Scheme 1) that exhibit two absorption maxima at 451 and 580 nm, the second one being more intense, and bleach back to the uncoloured closed form upon neutralization with Et_3N. The parent compound **6**, substituted by a CH_2OH group shows a similar behavior developing a violet colouration characterized by two maxima at 449 and 581 nm. The new compounds **3–5,** uncoloured in $CHCl_3$, develop deep violet to blue colourations after the addition of a few drops of trifluoroacetic acid (TFA) (Table 1).

The introduction of bromine or *p*-(hydroxymethyl)phenyl group on the C-*sp* [3] phenyl group (compounds **3a, 5a**) has a very limited effect on the λ_{max} of the open form, when compared with compounds **1** and **6**, which indicates that in the coloured cationic species these substituents are not conjugated with the rest of the molecule, adopting probably a perpendicular disposition. Therefore the introduction of the linkage in this position does not perturb the photochromic properties of the core molecule (Scheme 2). As expected, the introduction of a bromine or *p*-(hydroxymethyl)phenyl in the position 7 of the naphthofuran (compounds **3b**, **5b**) induces a significant bathochromic shift of the λ_{max} of the cationic open form (12–20 nm). Thus, the protonation of compound **3b** generates a coloured species with two absorption maxima at 439 and 592 nm corresponding to a dark bluish colouration (Fig. 4).

Table 1
Maxima wavelength of absorption of naphthofurans **1, 3–6** (5.0×10^{-5} M, $CHCl_3$) before and after TFA addition.

Compound	Substituents	λ_{max} (nm) in $CHCl_3$	λ_{max} (nm) after TFA addition
1	H	373	451, 580
6	7-CH_2OH	373	449, 581
3a	*p*-BrPh	373	442, 583
5a	*p*-PhPhCH_2OH	373	451, 582
3b	7-Br	381	439, 592
5b	7-PhCH_2OH	381	458, 600
3c	7-Br; PhOMe	381	455, 660
4c	7-Ph; PhOMe	381	468, 663
5c	7-Ph; PhOH	381	458, 663

The presence of a *p*-methoxyphenyl group in the allene function and a phenyl in the position 7 of the naphthofuran (compounds **3c, 4c, 5c**) induces also a noteworthy bathochromic shift, particularly in the second absorption maxima of the cationic species (Fig. 5). The species formed after protonation of compound **4c** is green with the maxima at 468 nm (+17 nm) and 663 nm (+83 nm). Upon NEt_3 addition these coloured species are converted back to the initial naphthofuran although a slightly residual absorption near 420 nm

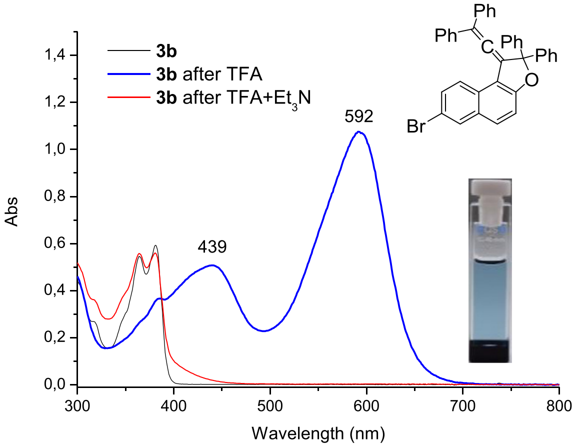

Fig. 4. Absorption spectra of naphthofuran **3b** before (black), after the addition of CF_3COOH (blue) and after the subsequent addition of NEt_3 (red).

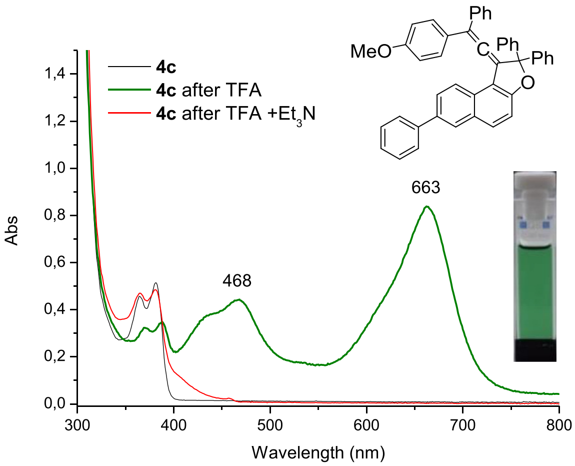

Fig. 5. Absorption spectra of naphthofuran **4c** before (black), after the addition of CF_3COOH (green) and after the subsequent addition of NEt_3 (red).

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can be observed in almost all compounds (Figs. 4 and 5).

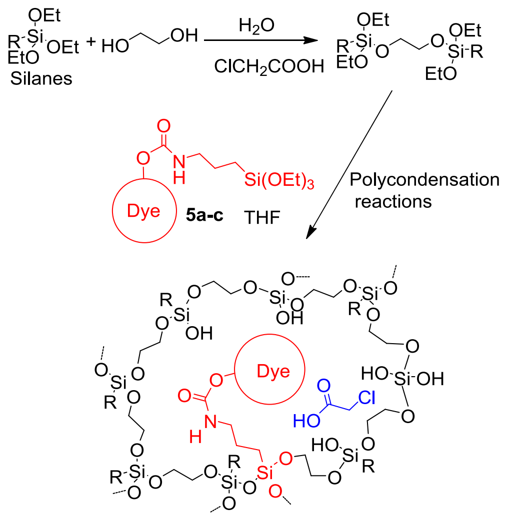
2.4. Photochromism

The colour change associated with the photochromic phenomena is due to a significant change in the molecules structure which causes an increase in the conjugation and consequently in the λ_{max}^{10}. This transformation requires space to occur and therefore the photochromic phenomena is rarely observed when the molecules are in solid state, being more common in solution or when the molecules are dispersed in polymeric matrices [11]. Naphthofurans operate particularly well when adsorbed in acidic silica gel producing a non-transparent white photochromic powder sensible to the sunlight, at room temperature, but are not active in common polyacrylate and polyurethane polymers used with naphthopyrans. We have found that organically modified silica materials are especially adequate to accumulate the naphthofurans, are compatible with an acidic environment and generate transparent and flexible materials whose properties can be tuned either through the change in the fabrication conditions or in the structure of the siloxane precursors [6,7].

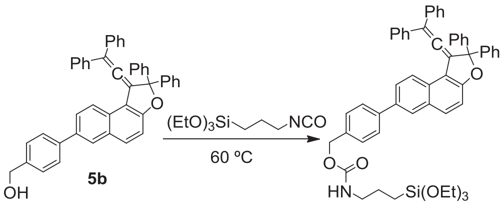
The best results have been obtained starting from mixtures of tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), phenyltriethoxysilane (PTES), 1,2-ethanediol, chloroacetic acid, water, THF and the photochromic compound. The sol obtained after stirring these precursors at room temperature, is cured, at 50 °C, for several days affording an uncoloured transparent photochromic solid material. During the hydrolysis and condensation reactions of the precursors a three dimensional siloxane porous network is formed in which the chloroacetic acid and the photochromic molecule are retained, while the solvents are expelled [10].

However, we have noticed that during the curing process the naphthofurans tend to precipitate as the space within the porous structure decreases. To avoid this it is preferable to introduce a reactive siloxane chain in the compounds which allows them to become part of the siloxane network (Scheme 6) [7].

Thus, before adding the photochromic dyes **5a-c, 6** to the sol, these compounds, possessing reactive hydroxyl groups, were treated with 3-(triethoxysilyl)propyl isocyanate at 60 °C for 7 days affording the respective silanized compounds, which, due to their high reactivity under acidic conditions, were not purified and used as such in the preparation of the doped ormosil materials (Scheme 7).



Scheme 6. Model of the siloxane material doped with the photochromic dyes.



Scheme 7. Silanization of the vinylidene-naphthofuran **5b**.

To prepare the photochromic materials a solution of TEOS/MTES/PTES/1,2-ethanediol/water/chloroacetic acid (1/1/1/3.4/4.2/0.48 M ratio) was stirred at 25 °C for 7 h and then a solution of the silanized photochromic compounds **5a-c, 6** in THF was added (0.025 M ratio). The resulting sol was transferred into a petri dish and cured at 50 °C for 7 days affording transparent solid disks with 1.0 mm thickness. Once the materials were removed from the oven some cracks appeared.

The transparent uncoloured siloxane matrix has no relevant absorption in the UV region between 300 and 400 nm. The materials doped with the silanized compounds **5a-c, 6** were all uncoloured in the dark. The UV—vis spectra of the materials doped with the silanized naphthofurans **5a-c**, **6** (Fig. 6) show that, in solution, the compounds substituted by an aromatic group in the 7 position (**5b,c**) absorb at higher wavelengths than the reference compound **6**, while, in the matrix, the opposite situation occurs: the substituted naphthofurans **5b,c**, absorb at lower wavelengths which indicates that probably, in the thick matrix, the extra aromatic ring in the naphthalene group adopts preferentially a perpendicular configuration preventing conjugation.

The uncoloured materials doped with the silanized naphthofurans **5a-c**, **6** were exposed to a UV lamp (370 nm, 36 W) for 2 min. All materials developed a light colouration with ΔAbs between 0.16 and 0.33 (Table 2). The UV—vis spectra of the materials doped with the silanized reference compound **6** show, after UV exposure, the development of two bands near 450 and 576 nm in accordance with the behavior observed in solution after addition of a strong acid. The material doped with compound **5a**, exhibit also the same expected behavior (maxima at 450 and 578 nm) with a violet colouration.

The introduction of a phenyl group in the 7 position (compound **5b**) generates a bathochromic shift (+20 nm) of the second band: the material doped with this compound develops a bluish

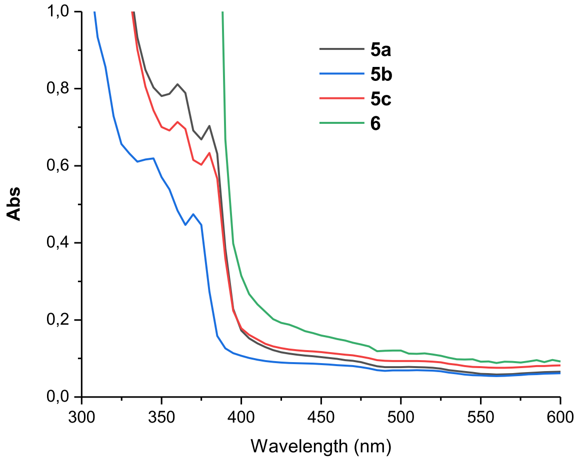


Fig. 6. UV— vis spectra of the materials doped with the silanized compounds **5a-c** and **6**.

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Table 2
Photochromic properties of the materials doped with compounds **5a-c, 6** after UV exposure (2 min): Absorption maxima, colour, absorbance variation, bleaching rate constants, half-life times ($t_{1/2}$) and $t_{3/4}$.

Compound	λ_{max} (nm) under UV	Colour	Abs	k_1 (min^{-1}); k_2 (min^{-1})	$t_{1/2}$ (min)	$t_{3/4}$ (min)
6	450, 576	violet	0.33	0.38; 0.066	3.11	8.89
5a	450, 578	violet	0.16	0.34; 0.064	3.11	8.74
5b	457, 595	blue	0.21	0.39; 0.064	3.18	9.75
5c	458, 606	green	0.17	0.37; 0.054	3.35	11.09

colouration characterized by two bands at 457 and 595 nm, which are comparable to those observed by acidochromism (Fig. 7, Table 1).

However, while the addition of acid to a $CHCl_3$ solution of compound **4c,** substituted with a phenyl group in the 7 position and a methoxyphenyl group in the allene, leads to a large bathochromic shift of the maxima wavelength (maxima at 468 and 663 nm), the material doped with the parent silanized compound **5c** develop, after UV exposure, two bands at lower wavelengths (458 and 606 nm) indicating a less efficient conjugation in the matrix. Therefore the behavior observed in solution is not completely transmitted to the matrix (Fig. 8).

When the light source was removed the materials lose progressively their colouration following a bi-exponential decay with two rate constants of similar amplitude, the second being 6–7 times slower than the first (Fig. 9, Table 2). This means that there is initially a fast colour decay followed by a slower colour fading. According, the materials exhibit an half-life time of 3 min and an higher $t_{3/4}$ (9–11 min). However, after 15 min the materials have lost approximatively 80% of their colouration and the residual colour is undetectable by the human eye. This process can be repeated several times in the same day without significant changes in the behavior although after a few days the photochromic properties tend to be attenuated. The materials show a comparable behavior under sunlight, although the colour intensities were slightly lower.

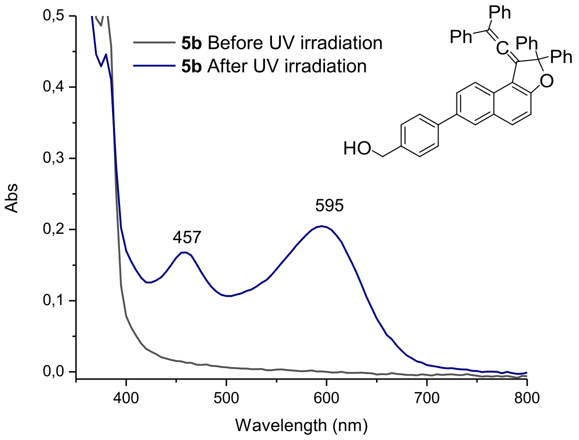

Fig. 7. UV– Vis spectra of the material doped with the silanized naphthofuran **5b** before and after UV exposure.

Fig. 8. Photos of the material doped with the silanized compound **5c** after total or partial exposure to the sunlight.

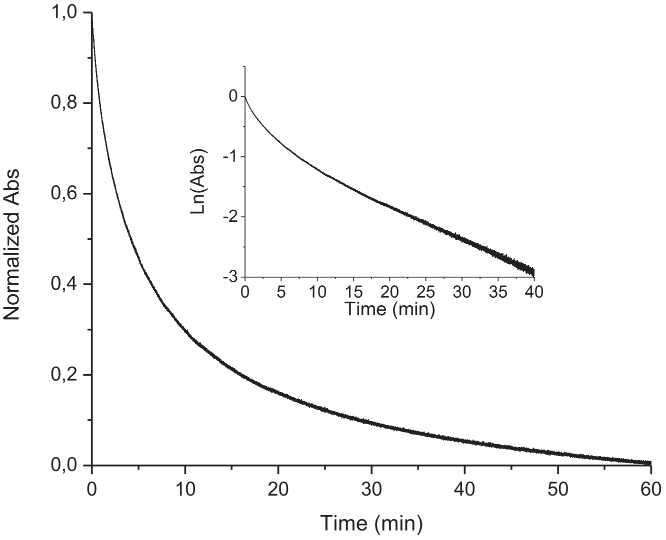

Fig. 9. Normalized fading kinetics of the material doped with silanized naphthofuran **5b** measured at 595 nm. Inset graphic (ln Abs vs time) shows the deviation from a monoexponential behavior.

3. Conclusion

A set of new vinylidene-naphthopyrans possessing an extra aromatic ring and a reactive hydroxyl function were easily prepared in 3 steps. These compounds were then silanized and embedded in a siloxane matrix producing transparent uncoloured photochromic materials that developed violet, green or bluish colourations when exposed to the UV or sunlight. The introduction of these substituents affects both the λ_{max} of absorption of the photochromic compounds in the closed (before UV) and open form (after UV) although the results observed in solution are not the same as those observed in the matrix. The introduction of an aromatic ring in the 7 position, compound **5b**, leads to a bathochromic shift in the λ_{max} of absorption of the closed form (381 nm) approaching the 400 nm limit, and also in the λ_{max} of absorption of the open form generating a bluish coloured species with two maxima at 458 and 600 nm. UV exposure of the material doped with this compound, for 2 min, generates a blue colouration that fades to the initial uncoloured state within 15 min.

4. Experimental section

4.1. General remarks

All reaction were monitored by thin-layer chromatography on aluminum plates coated with Merck silica gel 60 F254 (0.25 mm). IR spectra were obtained in a Shimadzu IRAffinity spectrometer using

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an ATR mode. Melting point were determined using a microscope URAC with a heating plate and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded at 298 K on a Bruker ARX 400 spectrometer (at 400.13 and 100.62 MHz). High resolution electrospray ionization time-of-flight (ESI-TOF) mass spectra and electron-impact ionization time-of-flight mass spectra were determined with a VG AutoSpec M spectrometer. Diol **2b** was prepared according to reference [4].

*4.2. General procedure for the synthesis of diols **2a-c***

n-Butyllithium (2 eq, 3.85 mL, 2.5 M in hexane) was added dropwise to a solution of 1,1-diarylprop-2-yn-1-ol (1.00 g; 4.8 mmol) in dry THF (25 mL) at 0 °C and the cold mixture was maintained under constant stirring for 30 min. The adequate benzophenone (1.1 eq) was added, at once, to the solution and the resulting mixture stirred at room temperature for 22 h. The solvent was removed, HCl (5%, 30 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 30 mL). The combined organic phases were dried (Na_2SO_4) and the solvent removed under reduced pressure to give an oil which was purified by recrystallization from CH_2Cl_2/petroleum ether.

*4.2.1. 1-(p-Bromophenyl)-1,4,4-triphenylbut-2-yne-1,4-diol (**2a**)*

Obtained from *p*-bromobenzophenone (1.87 g, 83%). Mp 117.3–120.1 °C. IR (KBr, cm^{-1}): 3408, 1596, 1492, 1442, 1395, 1208, 1127, 1073, 1013, 986, 892, 818, 745, 691, 611. ^{1}H NMR (400 MHz, $CDCl_3$): 7.60–7.50 (m, 6H), 7.50–7.40 (m, 4H), 7.35–7.20 (m, 9H), 3.11 (s, 1H), 3.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.5, 144.2, 143.8, 131.4, 128.4, 128.3, 128.0, 127.9, 127.8, 125.9, 125.8, 121.8, 90.3, 89.4, 74.5, 74.1. EI-MS (TOF) *m*/*z* (%): 450 (M$^+$-18, 8), 436 (31), 434 (35), 347 (8), 276 (15), 267 (10), 265 (35), 263 (14), 207 (22), 189 (15), 184 (18), 182 (18), 178 (28), 165 (19), 105 (100). HRMS calcd for $C_{28}H_{19}OBr$ (M-H_2O): 450.0619, found: 450.0619.

*4.2.2. 1,1,4,4-Tetraphenylbut-2-yne-1,4 diol (**2b**)*

Obtained from benzophenone (1.51 g, 81%). Mp: 201.4–203.0 °C. IR (KBr, cm^{-1}): 3532, 3456, 3061, 3019, 2918, 2843, 2364, 2339, 1600, 1499, 1448, 1331, 1213, 1138, 1070, 1028, 995, 911, 886, 776, 743, 693, 642, 609. ^{1}H NMR (400 MHz, $CDCl_3$): 7.59 (d, *J* = 7.9 Hz, 8H), 7.39–7.23 (m, 12H), 2.86 (s, 2H, OH). EI-MS (TOF) *m*/*z* (%): 372 (M$^+$-18, 32), 371 (11), 370 (14), 356 (28), 344 (22), 267 (22), 265 (27), 252 (11), 208 (10), 207 (14), 182 (64), 181 (10), 179 (13), 178 (17), 165 (19), 05 (100), 77 (50). HRMS calcd for $C_{28}H_{20}O$ (M - H_2O): 372.1514, found: 372.1503.

*4.2.3. 1-(p-Methoxyphenyl)-1,4,4-triphenylbut-2-yne-1,4-diol (**2c**)*

Obtained from *p*-methoxybenzophenone (1.43 g, 71%). Mp 106.4–108.8 °C. IR (KBr, cm^{-1}): 3375, 1590, 1509, 1446, 1362, 1241, 1174, 996, 892, 839, 778, 691. ^{1}H NMR (400 MHz, $CDCl_3$): 7.59–7.50 (m, 6H), 7.35 (d, *J* = 7.1 Hz, 2H), 7.32–7.26 (m, 9H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H, OCH_3), 3.03–2.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.1, 144.8, 144.7, 137.0, 128.3, 128.7, 127.8, 127.7, 127.4, 126.0, 125.9, 113.6, 90.2, 89.8, 74.5, 74.2, 55.3. EI-MS (TOF) *m*/*z* (%): 420 (M$^+$, 18), 225 (31), 386 (100), 374 (28), 143 (47), 265 (31), 252 (26), 237 (26), 207 (14), 182 (14), 165 (38). HRMS calcd for $C_{29}H_{24}O_3$: 420.1725, found: 420.1724.

*4.3. General procedure for the synthesis of vinylidene-naphthofurans **3a-c***

A solution of naphthol (2.38 mmol), tetraarylbut-2-yn-1,4-diol **2a-c** (1 eq), *p*-TSA (catalytic) in $CHCl_3$ (20 mL) was stirred 5 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by recrystallization from CH_2Cl_2/ethanol.

*4.3.1. 2-(4-Bromophenyl)-1-(2,2-diphenylvinylidene)-2-phenyl-1,2-dihydronaphtho[2,1-b]furan (**3a**)*

Slightly yellow solid obtained from 2-naphthol and diol **2a** (0.96 g, 78%). Mp 183.5–188.0 °C. IR (cm^{-1}): 3054, 3027, 1624, 1591, 1518, 1490, 1251, 960, 809, 750, 690. ^{1}H NMR (400 MHz, $CDCl_3$): 8.27 (d, *J* = 5.5 Hz, 1H), 7.90–7.80 (m, 2H), 7.49 (d, *J* = 5.0 Hz, 2H), 7.47 (d, *J* = 5.0 Hz, 2H), 7.40–7.25 (m, 15H), 7.21 (m, 1H), 7.15 (m, 1H), 6.96 (d, *J* = 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 202.7, 157.6, 142.5, 142.1, 136.2, 131.9, 131.5, 131.2, 130.2, 130.1, 129.7, 129.1, 129.0, 128.7, 128.5, 128.4, 128.0, 127.9, 127.8, 127.4, 127.2, 127.1, 123.8, 122.2, 122.0, 117.6, 114.6, 113.3, 112.3, 94.3. EI-MS (TOF) *m*/*z* (%): 578 ([M+2]$^+$, 100), 576 (M$^+$, 98), 501 (44), 499 (45), 420 (84), 391 (29), 331 (33), 313 (85), 302 (41), 165 (41). HRMS calcd for $C_{38}H_{25}OBr$: 576.1089, found: 576.1080.

*4.3.2. 7-Bromo-1-(2,2-diphenylvinylidene)-2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan (**3b**)*

Slightly yellow solid obtained from 6-bromonaphth-2-ol and diol **2b** (0.86 g, 97%). Mp 251.2–253.5 °C. IR (cm^{-1}): 3083, 3058, 3026, 1568, 1507, 1270, 952, 760, 688. ^{1}H NMR (400 MHz, $CDCl_3$): 8.10 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 1.8 Hz, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.52 (m, 1H), 7.42 (m, 4H), 7.30–7.15 (m, 13H), 7.11 (dd, *J* = 7.2 Hz, *J* = 1.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 202.6, 157.93, 142.7, 136.2, 131.2, 131.0, 130.9, 130.7, 128.7, 128.4, 128.21, 128.15, 128.0, 127.8, 127.2, 123.8, 117.6, 117.2, 114.4, 113.8, 113.5, 95.0. EI-MS (TOF) *m*/*z* (%): 578 ([M+2]$^+$, 71), 576 (M$^+$, 76), 501 (40), 499 (45), 420 (100), 409 (26), 313 (57), 300 (26), 165 (44). HRMS calcd for $C_{38}H_{25}OBr$: 576.1089, found: 576.1081.

*4.3.3. 7-Bromo-1-(2-(4-methoxyphenyl)-2-phenylvinylidene)-2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan (**3c**)*

Slightly yellow solid obtained from 6-bromonaphth-2-ol and diol **1c** (1.06 g, 73%). Mp 222.2–224.4 °C. IR (cm^{-1}): 3068, 3025, 2956, 2834, 1572, 1504, 1443, 1242, 1161, 1037, 961, 880, 809, 697. ^{1}H NMR (400 MHz, $CDCl_3$): 8.10 (d, *J* = 8.9 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.52 (dd, J = 8.9, *J* = 1.5 Hz, 1H), 7.44–7.39 (m, 4H), 7.30–7.20 (m, 11H), 7.11 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 202.3, 159.40, 157.9, 142.9, 142.8, 136.5, 131.2, 130.9, 130.7, 129.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 126.8, 123.8, 117.2, 114.2, 114.0, 113.9, 113.5, 95.0, 55.3. EI-MS (TOF) *m*/*z* (%): 608 ([M+2]$^+$, 99), 606 (M$^+$, 100), 531 (52), 529 (56), 450 (56), 313 (24), 300 (38), 289 (33), 197 (70). HRMS calcd for $C_{39}H_{27}O_2Br$: 606.1194, found: 606.1196.

*4.4. General procedure for the synthesis of naphthofurans **5a-b, 4c***

A mixture of naphthofuran **3** (1,15 mmol), boronic acid (1,76 mmol), $Pd(PPh_3)_4$ (40 mg; 0.0346 mmol) in toluene (3 mL), ethanol (3 mL) and K_2CO_3 (aqueous 2 M solution, 3 mL) was heated under reflux for 4–5 h. The black solution was filtered, water (10 mL) was added, and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried (Na_2SO_4), filtered, and the solvent removed under reduced pressure to provide an oil which was purified by recrystallization from CH_2Cl_2/ethanol.

*4.4.1. 1-(2,2-Diphenylvinylidene)-2-(p-hydroxymethylbiphenyl)-2-phenyl-1,2-dihydronaphtho[2,1-b]furan (**5a**)*

Obtained from naphthofuran **3a** and phenylboronic acid (0.49 g, 79%). Orange crystals. Mp 80.3–84.7 °C. IR (cm^{-1}): 3310, 3054, 3022, 2928, 1623, 1491, 1269, 1247, 958, 807. ^{1}H NMR (400 MHz, $CDCl_3$): 8.25 (d, *J* = 8.6 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 2H), 7.65 (m, 1H),

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7.61–7.4 (m, 6H), 7.4–7.1 (m, 17H), 4.73 (s, 2H), 1.6 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 202.8, 157.8, 142.8, 142.2, 140.5, 140.1, 140.0, 136.4, 132.1, 132.0, 131.8, 130.0, 129.1, 129.0, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.41, 127.38, 127.3, 126.9, 123.6, 122.2, 117.4, 114.8, 113.4, 112.4, 94.9, 65.0. EI-MS (TOF) *m/z* (%): 604 (M^+, 19), 602 (31), 588 (10), 525 (27), 498 (18), 421 (31), 313 (28), 277 (100), 201 (25). HRMS calcd for $C_{45}H_{32}O_2$: 604.2402, found: 604.2410.

4.4.2. *7-Hydroxymethyl-1-(2,2-diphenylvinylidene)-2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan* ***5b***

Obtained from naphthofuran **3b** and *p*-(hydroxymethyl)phenylboronic acid. Yellowish crystals (88 mg, 84%). Mp 229.3–231.2 °C. IR (cm^{-1}): 3564, 3053, 3026, 1596, 1508, 1253, 958, 805. ^{1}H NMR (400 MHz, $CDCl_3$): 8.33 (d, $J = 8.6$ Hz, 1H), 8.05 (d, $J = 1.4$ Hz, 1H), 7.87 (d, $J = 8.8$ Hz, 1H), 7.76 (dd, $J = 8.7$ Hz, $J = 1.5$ Hz, 1H), 7.69 (d, $J = 8.1$ Hz, 2H), 7.6–7.4 (m, 6H), 7.3–7.1 (m, 17H), 4.77 (s, 2H), 1.6 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 202.8, 157.9, 142.9, 140.3, 139.7, 136.4, 135.9, 132.0, 130.3, 128.9, 128.7, 128.4, 128.1, 127.9, 127.7, 127.5, 127.32, 127.27, 126.8, 122.7, 117.4, 114.7, 113.5, 112.9, 94.9, 65.0. EI-MS (TOF) *m/z* (%): 604 (M^+, 6), 602 (36), 588 (16), 525 (31), 510 (14), 435 (12), 395 (17), 368 (41), 353 (30), 255 (27), 213 (42). HRMS calcd for $C_{45}H_{32}O_2$: 604.2402, found: 604.2390.

4.4.3. *1-(2-(4-Methoxyphenyl)-2-phenylvinylidene)-2,2,7-triphenyl-1,2-dihydronaphtho[2,1-b]furan (**4c**)*

Obtained from naphthofuran **3c** and phenylboronic acid. Grey crystals (0.59 g, 85%). Mp 179.9–183.6 °C. IR (cm^{-1}): 3058, 3001, 2957, 2832, 1592, 1508, 1240, 1171, 944, 828, 771, 692. ^{1}H NMR (400 MHz, $CDCl_3$): 8.35 (d, $J = 8.6$ Hz, 1H), 8.06 (s, 1H), 7.88 (d, $J = 8.8$ Hz, 1H), 7.77 (d, $J = 8.7$ Hz, 1H), 7.70 (d, $J = 7.7$ Hz, 2H), 7.54–7.40 (m, 6H), 7.40–7.20 (m, 13H), 7.10 (d, $J = 8.7$ Hz, 2H), 6.82 (d, $J = 8.7$ Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 202.5, 159.3, 157.9, 143.1, 143.0, 140.9, 136.7, 136.3, 131.9, 130.3, 129.9, 128.9, 128.8, 128.7, 128.6, 128.4, 128.1 (2C), 127.9, 127.7, 127.4, 127.2, 127.1, 126.9, 122.7, 117.0, 114.5, 113.81, 113.7, 112.8, 94.9, 55.3. EI-MS (TOF) *m/z* (%): 604 (M^+, 82), 573 (12), 527 (100), 511 (9), 496 (19), 407 (12), 376 (17), 363 (14), 300 (11), 289 (12). HRMS calcd for $C_{45}H_{32}O_2$: 604.2402, found: 604.2428.

4.4.4. *1-(2-(4-Hydroxyphenyl)-2-phenylvinylidene)-2,2,7-triphenyl-1,2-dihydronaphtho[2,1-b]furan (**5c**)*

BBr_3 (1.0 M; 0.33 mL) was added to a solution of naphthofuran **4c** (0.20 g; 0.33 mmol) in dry CH_2Cl_2 (15 mL) at room temperature. After stirring for 5 h water (15 mL) was added to the green dark solution and the aqueous phase extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phases were dried (Na_2SO_4), filtered and the solvent removed under reduced pressure to provide an oil which was purified by column chromatography using 15% EtOAc/petroleum ether. The compound was further purified by recrystallization from CH_2Cl_2/petroleum ether to afford white crystals (0.15 g, 76%). Mp 120.3–124.7 °C. IR (cm^{-1}): 3347, 3060, 3023, 1597, 1495, 1448, 1264, 1167, 1024, 952, 755. ^{1}H NMR (400 MHz, $CDCl_3$): 8.29 (d, $J = 8.6$ Hz, 1H), 8.01 (s, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.65 (d, $J = 7.9$ Hz, 2H), 7.5–7.35 (m, 6H), 7.35–7.10 (m, 17H), 7.01 (d, $J = 8.3$ Hz, 2H), 6.70 (d, $J = 8.5$ Hz, 2H), 4.8 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 202.4, 157.9, 155.3, 143.1, 142.9, 140.9, 136.6, 136.3, 131.9, 130.3, 130.1, 128.9, 128.8, 128.7, 128.4, 128.12, 128.09, 127.9, 127.7, 127.4, 127.2, 127.1, 126.9, 122.6, 116.9, 115.3, 114.5, 113.6, 112.8, 94.9. EI-MS (TOF) *m/z* (%): 590 (M^+, 62), 512 (100), 496 (17), 407 (16), 183 (11). HRMS calcd for $C_{44}H_{30}O_2$: 590.2246, found: 590.2238.

4.5. *Preparation of the photochromic materials*

A solution of naphthofuran **5a-c, 6** (0.160 g), 3-(triethoxysilyl) propyl isocyanate (1eq) in dry THF was stirred at 50–60 °C for 7 days. The solvent was removed at reduced pressure and residue dried under high vacuum affording the corresponding silanized naphthofurans that were not purified. A mixture of triethoxymethlysilane (1117 μL, 5.5 mmol), tetraethoxysilane (1248 μL, 5.5 mmol), phenyltriethoxysilane (1355 μL, 5.5 mmol), ethylene glycol (1047 μL, 18.72 mmol), chloroacetic acid (250 mg, 2.65 mmol) and water (420 μL, 23 mmol) was stirred for 7 h at 25 °C and then a solution of the above silanized naphthofurans (20 mg, 0.025 mmol) in THF (730 μL) was added and this solution and maintained in vigorous stirring for 30 min. The solution was then transferred to a petri dish and kept covered, in an oven at 50 °C. After 4 days, the petri dish was uncovered and maintained at 50 °C for more 3 days providing a transparent material.

4.6. *Measurement of the photochromic properties*

The UV–Vis spectra of the materials, before and after UV irradiation was recorded using a UV–Vis spectrophotometer (CARY 50 Varian). To activate the molecules an UV lamp (370 nm, 36 W) was positioned over the samples and the UV light was switch on for 2 min producing a violet/green colouration. 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 rate constant (k) was calculated by the fitting of the bleaching curves to a bi-exponential decay equation: $A = A_0 + A_1.\exp(-k_1 t) + A_2.\exp(-k_2 t) +$ where A_0 is the initial absorbance of the sample before UV irradiation and k_1 and k_2 two rate constants.

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References

[1] H. Bouas-Laurent, H. Dürr, Pure Appl. Chem. 73 (2001) 639–665.
[2] S. Nigel Corns, S.M. Partington, A.D. Towns, Color. Technol. 125 (2009) 249–261.
[3] A.D. Towns, in: G. Bergamini, S. Silvi (Eds.), Applied Photochemistry - when Light Meets Molecules, Springer international Publishing, 2016, pp. 227–279.
[4] C.M. Sousa, J. Berthet, S. Delbaere, P.J. Coelho, J. Org. Chem. 78 (2013) 6956–6961.
[5] C.M. Sousa, J. Berthet, S. Delbaere, P.J. Coelho, Dyes Pigments 137 (2017) 593–600.
[6] R. Sagheer, M.S. Rafique, F. Saleemi, S. Arif, F. Naab, O. Toader, A. Mahmood, R. Rashid, I. Hussain, Mater. Sci. Poland 34 (2016) 468–478.
[7] R. Pardo, M. Zayat, D. Levy, Chem. Soc. Rev. 40 (2011) 672.
[8] C.M. Sousa, A. Polónia, P.J. Coelho, Prog. Org. Coating 125 (2018) 146–152.
[9] T.V. Pinto, C.M. Sousa, C.A.D. Sousa, M.M. Aboelhassan, A.F. Peixoto, C. Pereira, P.J. Coelho, C. Freire, Dalton Trans. 46 (2017) 9076–9087.
[10] R. Pardo, M. Zayat, D. Levy, Compt. Rendus Chem. 13 (2010) 212–226.
[11] P.J. Coelho, L.M. Carvalho, L.F.F.F. Gonçalves, C.J.R. Silva, A.M. Campos, M. Jesus Gomes, J. Sol. Gel Sci. Technol. 56 (2010) 203–211.

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