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Spectrokinetic studies on new bi-photochromic molecules containing two naphthopyran entities

Paulo J. Coelho,^{a,*} Maria A. Salvador,^a B. Mark Heron^b and Luis M. Carvalho^a

^aCentro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-911 Vila Real, Portugal ^bDepartment of Colour Chemistry, The University of Leeds, Leeds LS2 9JT, UK

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Abstract—A range of new bi-photochromic molecules containing two identical (**3a**–**d**) or two distinct naphthopyran units (**6a**–**d**), linked through the phenyl substituents located on the sp³ hybridised pyran ring carbon atom, using conjugated and non-conjugated spacers, have been synthesised from bis-propynols and (substituted)naphthols. Study of the spectrokinetic properties of these compounds under near UV–vis continuous irradiation conditions revealed that the two naphthopyran units are stimulated independently leading to open forms with higher colourabilities but without affecting the individual bleaching kinetics. Compared to the individual photochromic components and to model mono-photochromes it was observed that the nature of the bridge has a small effect on the photochromic properties of each system. © 2005 Elsevier Ltd. All rights reserved.

1. Introduction

The photochromic properties of naphthopyrans have been extensively studied in the last decade due to the wide range of applications with prominence in the manufacture of ophthalmic plastic lenses and solar protection glasses.¹ Under near-UV light irradiation these uncoloured or faintly coloured molecules, either in solution or incorporated in polymeric matrices, undergo an electrocyclic pyran-ring opening with cleavage of the $C(sp^3)$ –O bond and a subsequent structural reorganisation allowing the photogenerated species to adopt more planar structures (the so-called 'open form', OF) with greater conjugation, which is responsible for the increased absorption in the visible part of the spectrum (Scheme 1). The OF is constituted by a set



Scheme 1.

of coloured stereoisomers, with similar absorption characteristics but with diverse thermal stabilities.² Under continuous near-UV irradiation a photostationary equilibrium is attained between the uncoloured 'closed form' (CF) and the OF leading to a colour change of the system. When the light source is removed the equilibrium shifts and the system returns to the original colourless state, either via a thermal or a photoinduced process, with light of different wavelength from the first, unveiling the reversible colour behaviour that is characteristic of this photochromic system. UV and NMR studies revealed that at room temperature the main photoproducts are the TC and TT isomers (Scheme 1), the latter being the most thermally stable.³

A great number of substitutions and/or annelations have been studied in the naphthopyran family in order to increase the ability to produce intense coloured forms (colourability), to tailor chromatic properties or to change fading rates of these systems.^{4–6} Consequently, there has been a significant increase in patenting of new molecules and systems, although many exaggerated claims were made about their performances. Nevertheless, significant improvements were attained and many commercially interesting photochromic systems were discovered. An important advancement is related to the colour range achievable with naphthopyrans that, initially, was limited to orange/yellow colours and nowadays is extended to virtually any colour.

This feature is particularly important for photochromic lens manufacturers because the optical lens market is dominated by neutral colours (browns and greys). In principle, neutral

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^{*} Corresponding author. Tel.:+351 259 350284; fax: +351 259 350480; e-mail: pcoelho@utad.pt



Scheme 2.

colours can be produced by mixing two or more photochromic dyes that allow a constant coverage of an extended range of the visible spectrum (usually 420-620 nm is acceptable). This approach meets the goal, although it opens a set of serious problems, beyond the position of the absorption maxima and the shape of the absorption bands in the visible and UV (activating) spectral range. To prevent photochromic lenses from displaying different colours under varying exposure conditions the photochromic dyes should have similar (within some tolerance limits) photochromic properties. These include the colouring and fading kinetics, temperature dependence, solvatochromic effects and fatigue resistance. The mixture of the lesser possible number of photochromes belonging to the same family seems to be recommended. Several interesting formulations were developed and can be found in the patent literature.⁷

A second and highly desired approach to obtain neutralcolouring articles, because all the matching problems are overcome and the formulation processes would obviously be simpler, involves the use of a single photochromic dye with the desired absorption properties: at least two absorption bands conveniently spaced ($\Delta\lambda \sim 100-130$ nm) in the visible spectrum, of approximately equal intensity. Such molecules can be, in principle, obtained through appropriate substitution/annelation of the naphthopyran moieties, but in the literature few examples are described.^{8–10}

Recently, molecular structures involving the coupling of conveniently selected photochromes (e.g., naphthopyrandiarylethene,¹¹ naphthacene-diarylethene,¹²⁻¹³ diarylethene-dihydroazulene,¹⁴ naphthopyran-naphthopyran,¹⁵⁻¹⁸ spirooxazine-spirooxazine,^{17,19-20} naphthopyran-spirooxazine^{15,17,21}) through a covalent linkage have received some attention.

Studies on bi-photochromic supermolecules including



naphthopyran units, linked through their naphthalene units, revealed that although the kind of molecular spacer nature is critical and fading rates are sometimes affected, the simultaneous activation of both photochromic systems is possible. Alkyl (ethane), ester (Scheme 2), or acetylenic bridges did not substantially change the photochromic behaviour exhibited by the components taken individually and an additive effect was observed.^{15–16}

On the other hand, ethylenic spacers lead to supermolecules, which exhibit a complex and contradictory behaviour (Scheme 3).^{2,17–21} Some compounds with (*Z*)-ethylenic bonds exhibited thermally irreversible photochromic properties, and upon UV irradiation thermally stable coloured forms that persist from days to several weeks in the dark were formed, while others exhibited a thermally reversible behaviour, which can be considered as the superposition of the properties of the individual systems taken separately. With some bi-naphthopyrans it was observed that only one pyran unit was opened under UV irradiation, indicating a possible de-activation of one photochrome due to the presence of the other in the same framework.

Another approach involves the linkage of the two naphthopyrans thought one of the geminal aryl aromatic substituents. Recently, some interesting results have been obtained on bi-photochromic supermolecules with two naphthopyrans sharing a bi-thiophene unit linked through the two pyran ring sp³ C atoms (Scheme 3). These molecules showed a very significant bathochromic shift of the maximum wavelength of absorption of the OF and high colourabilities due to the extension of π -conjugation and the opening of both photochromic systems.^{22–23}

In the present paper, we report our results on the study of new bi-photochromic molecules obtained through the linkage of the naphthopyran sp³ phenyl substituents, using conjugated and non-conjugated spacers, including a shared aromatic ring (Scheme 4).





6d

Scheme 4.

2. Results and discussion

2.1. Synthesis

The bi-photochromic compounds 6a-d were prepared in

four steps starting from aromatic diketones 1a-c, which were commercially available (1b) or readily prepared by Friedel-Crafts benzoylation of diphenyl ether or dibenzyl (Scheme 5).²⁴ Treatment of diketones 1a-c with lithium trimethylsilylacetylide in THF followed by basic hydrolysis





Scheme 6.



Heating these diols with 0.8 equiv of 2-naphthol in 1,2-dichloroethane in the presence of an acid catalyst (pyridinium *p*-toluenesulphonate) and 2 equiv of trimethyl orthoformate, added as a dehydrating agent,²⁵ gave a mixture of symmetrical bi-naphthopyrans 3a-c (minor) and mono naphthopyrans 4a-c (major), with one reactive propargylic alcohol function still present, which were easily separated by column chromatography. Both compounds exhibit photochromic properties in solution at room temperature. Treating the mono naphthopyrans 4a-c with 1.1 equiv of 5-hydroxy-7*H*-benzo[*c*]fluoren-7-one, under the same reaction conditions, gave the naphthopyrans 5a-c. These compounds are highly coloured and possess two different covalently linked naphthopyrans entities, however, they show very weak photochromic properties due to the presence of the carbonyl function in the indene ring.⁴ Treatment of these compounds with a CH₃MgI solution gave, after hydrolysis, the new photochromic bi-naphthopyrans 6a-c in good yield (70-79%).

The same methodology was used to prepare the bi-naphthopyran **6d** from diol **2b** except that 1-naphthol was used instead of 2-naphthol (Scheme 6).

2.2. Photochromic properties

The photochromic behaviour of compounds **3–6** was studied in 10^{-4} M toluene solutions at 20 °C under continuous near UV–vis irradiation (150 W ozone free Xe lamp, light flux of 40 W m⁻², quartz cells, 1 cm light path, 3.5 ml of solution). Three spectrokinetic parameters, normally quoted when describing the properties of photochromic compounds, were evaluated: maximum wavelength of absorption of the open form (λ_{max}), thermal bleaching rates (k_{Δ}) and colourability (A_{eq}), estimated by the absorbance of the solution after reaching a photostationary equilibrium under the experimental conditions. The bleaching kinetics were studied in the dark, under thermal conditions. The data are summarised in Tables 1–4 where three reference compounds were included for comparison: **Ref1** (=3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran), **Ref2** (=3,3-diphenyl-13-methyl-13-hydroxy-3*H*-indeno[2,1-*f*]naphtho[1,2-*b*]pyran) and **Ref3** (=2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran).

2.2.1. Compounds 4a-d. Compounds 4a-c are 3,3diphenylnaphtho[2,1-b]pyran derivatives substituted at the para position of one of the 3-phenyl groups by an aryl substituted alkyl chain, 4b-c, or a conjugative electron donating group (OAr), 4a. The observed photochromic behaviours are characteristic of coloured forms of this family of compounds and, thus, similar to Ref1 (Table 1, Fig. 1): under continuous irradiation conditions, compounds 4a-c exhibit a single wide absorption band centered between 434–446 nm and weak colourabilities (0.2–0.3). After the removal of the UV irradiation source these compounds exhibit a bi-exponential colour decay with two very different fading rates: one fast $(0.07-0.09 \text{ s}^{-1})$ and another very slow $(2 \times 10^{-5}-6 \times 10^{-5} \text{ s}^{-1})$. As already referred these rate constants can be attributed, respectively, to the TC and TT open form isomers.³ Considering similar molar absorptivities for these isomers,² from the amplitudes

| Compounds | | | $\lambda_{max} (nm)$ | $A_{ m eq}$ | Residual colour ^a | $k_{\Delta} (s^{-1})$ |
|----------------|------------|--|----------------------|-------------|------------------------------|--|
| | Ref1 | | 432 | 0.27 | 0.06 | 6×10^{-2} (73) 7×10 ⁻⁶ (27) |
| OH CL OH | 4 a | L=PhOPh | 446 | 0.19 | 0.03 | 9×10^{-2} (74) 1×10^{-5} (26) |
| | 4b | L=Ph | 434 | 0.25 | 0.06 | $7 \times 10^{-2} (72)$ $2 \times 10^{-5} (28)$ |
| | 4c | $L = PhCH_2CH_2Ph$ | 438 | 0.25 | 0.05 | $7 \times 10^{-2} (73) \\ 6 \times 10^{-5} (27)$ |
| | 3a | L=PhOPh | 446 | 0.30 | 0.06 | $9 \times 10^{-2} (72)$ $3 \times 10^{-5} (28)$ |
| | 3b | L=Ph | 433 | 0.33 | 0.08 | $6 \times 10^{-2} (72)$ $4 \times 10^{-5} (28)$ |
| | 3c | $L = PhCH_2CH_2Ph$ | 438 | 0.42 | 0.09 | $\begin{array}{c} 8 \times 10^{-2} \ (78) \\ 4 \times 10^{-5} \ (22) \end{array}$ |
| | 5a | L=PhOPh | 438 ^b | 0.14 | 0.02 | $\begin{array}{c} 6 \times 10^{-2} \ (74) \\ 8 \times 10^{-4} \ (14) \\ 2 \times 10^{-4} \ (12) \end{array}$ |
| | 5b | L=Ph | 430 ^b | 0.21 | 0.05 | $5 \times 10^{-2} (55)$ $2 \times 10^{-2} (16)$ $8 \times 10^{-6} (29)$ |
| | 5c | L=PhCH ₂ CH ₂ Ph | 436 ^b | 0.17 | 0.03 | $8 \times 10^{-2} (66) 2 \times 10^{-2} (14) 4 \times 10^{-5} (20)$ |

Table 1. Spectrokinetic properties under continuous irradiation: maxima wavelengths of the coloured form (λ_{max}), colourability (A_{eq}), thermal bleaching rate (k_{Δ}) of compounds **3a–c**, **4a–c**, **5a–c** and **Ref1** in toluene solutions

^a Absorbance after 2000 s in the dark.

^b Shoulder. These measurements were not made at the λ_{max} because these solutions of compounds were already orange/red coloured before irradiation.

of the fading kinetics it can be deduced that the coloured OF is a mixture constituted mainly by the short lived TC isomer (72-73%), responsible for the initial fast colour decay, and by the more stable TT isomer (26-27%), which is responsible for the persistence of colour for a long time (Fig. 1). As expected, due to the presence of the *p*-substituent at the 3-phenyl group, the open forms are



Figure 1. Colour forming and colour bleaching at λ_{max} of Ref1, 3c and 4c.

slightly less thermally stable than **Ref1** and the observed lower colourabilities can be related to the faster ring closure kinetics, as these two parameters are inversely related.²⁶

Considering **Ref1**, compound **4a** exhibit the more pronounced bathochromic shift to the λ_{max} (+14 nm), although smaller that the one observed when the *p*-substituent is a methoxy group (+36 nm), reflecting the weaker electron donating character of the OAr group.²⁷

Similar results were obtained for compound 4d. This compound is a 2,2-diphenylnaphtho[1,2-*b*]pyran substituted at the *para* position of a 2-phenyl group and, as expected, its photochromic properties are very similar to **Ref3** (Table 2). It exhibits a maximum wavelength of absorption, λ_{max} , at 471 nm and two slow fading rates (7×10^{-4} and 2×10^{-6} s⁻¹) that are responsible for a very slow colour decay and therefore a high colourability (A_{eq} =1.1) (Fig. 2). The maximum absorbance obtained under UV exposition (A_{eq} = 1.0) was, however, considerably lower than the one obtained with **Ref3** (A_{eq} =1.5).

2.2.2. Compounds 3a–d. Compounds **3a–c** are bi-photochromic supermolecules with two naphtho[2,1-*b*]pyrans linked through conjugated (Ph) or non-conjugated chains

| Compounds | | λ_{\max} (nm) | $A_{\rm eq}$ | Residual colour ^a | $k_{\Delta} (s^{-1})$ |
|-----------|-----------------|-----------------------|--------------|------------------------------|--|
| | Ref3 | 470 | 1.5 | 0.36 | 6×10^{-4} (76) 1×10^{-6} (24) |
| он | 4d | 471 | 1.1 | 0.26 | $7 \times 10^{-4} (75) \\ 2 \times 10^{-6} (25)$ |
| | 3d | 480 | 2.7 | 0.94 | 5×10^{-4} (65) 7×10^{-7} (35) |
| | 5d ^b | 479 | 1.0 | 0.25 | $6 \times 10^{-4} (75)$ $2 \times 10^{-6} (25)$ |

Table 2. Spectrokinetic properties under continuous irradiation: maxima wavelengths of the coloured form (λ_{max}), colourability (A_{eq}), thermal bleaching rate (k_{Δ}) of compounds **3d**, **4d**, **5d**, and **Ref3** in toluene solutions

^a After 10000 s in the dark.

^b Solutions of this compound were already orange/red coloured before irradiation.

(PhOPh, PhCH₂CH₂Ph). Since the two sp³ aryl substituents are not equivalent many different coloured photoisomers can be expected to form. Relative to the λ_{max} and fading kinetics, it was observed a behaviour very similar to that recorded for the mono-photochromic molecules **4a–c** (Table 1, Figs. 1 and 3).

However, the maximum absorbances attained at the photostationary state (colourability) are significantly higher (Fig. 1) and as under our experimental conditions the colourability of 3,3-diphenyl-naphtho[2,1-b]pyran, **Ref1**, is

not linearly related to concentration (Fig. 4) one can infer that probably both pyran units were opened under exposure to UV. The increase of the residual absorbance at the end of the experiments corroborates this inference. Regarding the absorption wavelength of coloured forms of the model compounds $4\mathbf{a}-\mathbf{c}$ we can conclude that no additional extension of conjugation was achieved in the open forms of the bi-photochromic molecules, even considering **3b** where a phenyl group is shared by the two parts. This may indicate that, upon UV irradiation, both photochromic moieties are opened and the molecule adopts a conformation where each 'planar' open form is completely out of





Figure 2. Colour bleaching at λ_{max} of Ref3, 3d and 4d.

Figure 3. Normalized colour bleachings of Ref1, 3c, 4c and 5c.

| Compounds | | | λ_{\max} (nm) | A _{eq} | Residual colour ^a | $k_{\Delta} (s^{-1})$ |
|------------|----|--------------------|-----------------------|-----------------|------------------------------|---|
| | | Ref1 | 432 | 0.27 | 0.06 | 6×10^{-2} (73) 7×10^{-6} (27) |
| Me OH | | Ref2 | 533 419 | 1.3 0.71 | 0.21 | 3×10^{-3} (82) 5×10^{-6} (18) |
| | 6a | L=PhOPh | 425 | 0.85 | 0.10 | 7×10^{-2} (4) 5×10^{-3} (83) 1×10^{-5} (13) |
| | | | 536 | 1.4 | 0.19 | 5×10^{-3} (86) 1×10^{-5} (14) |
| | | | 423 | 0.76 | 0.12 | $\begin{array}{c} 4 \times 10^{-2} \ (6) \\ 3 \times 10^{-3} \ (78) \\ 2 \times 10^{-5} \ (16) \end{array}$ |
| | 6b | L=Ph | 533 | 1.3 | 0.22 | $3 \times 10^{-3} (82)$ $8 \times 10^{-6} (18)$ |
| | , | | 600 ^b | 0.62 | 0.07 | $3 \times 10^{-3} (87)$ $4 \times 10^{-5} (13)$ |
| | 6с | $L = PhCH_2CH_2Ph$ | 423 | 0.84 | 0.13 | $ \begin{array}{l} 6 \times 10^{-2} (6) \\ 4 \times 10^{-3} (78) \\ 2 \times 10^{-5} (16) \end{array} $ |
| | | | 533 | 1.3 | 0.20 | $4 \times 10^{-3} (83)$ $2 \times 10^{-5} (17)$ |
| \bigcirc | | | | | | |
| | | Ref1 + Ref2 | 420 | 0.85 | 0.15 | $\begin{array}{c} 6 \times 10^{-2} (11) \\ 3 \times 10^{-3} (70) \\ 2 \times 10^{-6} (19) \end{array}$ |
| | | | 528 | 1.2 | 0.22 | $5 \times 10^{-2} (2) 3 \times 10^{-3} (80) 5 \times 10^{-6} (18)$ |
| | | | | | | |

Table 3. Spectrokinetic properties under continuous irradiation: maxima wavelengths of the coloured form (λ_{max}), colourability (A_{eq}) thermal bleaching rate (k_{Δ}) of compounds **6a–c**, **Ref1**, **Ref2** and a equimolar mixture of **Ref1** and **Ref2**

^a Absorbance after 2000 s in the dark.

^b Wavelengths that do not correspond to λ_{max} .

plane of the other. The nature of the assayed bridges linking the two photochromic parts seems to have a negligible influence in the photochromic behaviour of these compounds.

Compound **3d** has two naphtho[1,2-*b*]pyran units linked by a common phenyl group. Exposure of this compound to UV light produced a band with a λ_{max} initially at 470 nm that gradually shifts to 480 nm until the photostationary state is attained (an inverse behaviour was observed during the bleaching). Compared to **Ref3** and the model compound **4d**, it can be observed a bathochromic shift (+10 nm) of the maximum wavelength of absorption that suggests that a phenyl (conjugative) bridge allows some extension of conjugation in the open form of this compound. The analysis of the bleaching kinetics revealed a bi-exponential behaviour, with close values for kinetic constants although with slightly different amplitudes (Table 2, Fig. 2). Relative to **Ref3** and **4d**, for compound **3d** the amplitude of the slower fading rate increased from 24 to 35% that points to an increase in the concentration of the TT species at the photostationary equilibrium. The colourability attained by this compound is nearly twice the one achieved by **Ref3** ($A_{eq} = 1.5$) and the residual colour (0.94) is much higher than those observed for **Ref3** (0.36) and **4c** (0.26) (Fig. 2). This additive behaviour unambiguously suggests the

| Compounds | | λ_{max} (nm) | $A_{ m eq}$ | Residual colour ^a | $k_{\Delta} (\mathrm{s}^{-1})$ |
|-----------|-----------|----------------------|-------------|------------------------------|--|
| Me OH | Ref2 | 533 419 | 1.3 0.71 | 0.21 | 3×10^{-3} (82) 5×10^{-6} (18) |
| | Ref3 | 470 | 1.5 | 0.36 | 6×10^{-4} (76) 1×10^{-6} (24) |
| — нс | | 472 ^a | 1.7 | 0.47 | 3×10^{-3} (23) 6×10^{-4} (49) 4×10^{-6} (28) |
| | 6d | 530 | 2.0 | 0.39 | 3×10^{-3} (48) 6×10^{-4} (31) 7×10^{-6} (21) |
| | | 620 ^a | 0.91 | 0.06 | 3×10^{-3} (78) 6×10^{-4} (14) 1×10^{-5} (8) |
| | | 470 ^a | 2.1 | 0.48 | $4 \times 10^{-3} (27) 6 \times 10^{-4} (50) 1 \times 10^{-6} (23)$ |
| | Ref2+Ref3 | 494 | 2.2 | 0.47 | $ \begin{array}{l} 4 \times 10^{-3} (35) \\ 6 \times 10^{-4} (44) \\ 2 \times 10^{-6} (21) \end{array} $ |
| | | 530 ^a | 2.1 | 0.50 | $4 \times 10^{-3} (27) 6 \times 10^{-4} (50) 1 \times 10^{-6} (23)$ |

Table 4. Spectrokinetic properties under continuous irradiation: maxima wavelengths of the coloured form (λ_{max}), colourability (A_{eq}) thermal bleaching rate (k_{Δ}) of compounds **6d**, **Ref2**, **Ref3** and a equimolar mixture of **Ref2** and **Ref3**

^a Wavelengths that do not correspond to λ_{max} .

independent opening of the two pyran rings in this molecule and the displacement of the λ_{max} with the irradiation time points to a consecutive opening of the pyran rings.

Considering **Ref3** a study of the effect of the concentration on the observed colourability, under our experimental conditions, displayed a linear relationship between A_{eq}



Figure 4. Colourability versus concentration for Ref1 and Ref3.

and concentration over a more extended concentration range (until 2×10^{-4} M) than for **Ref1** (Fig. 4). Obviously, at these concentrations, deviations from direct proportionality are strongly dependent upon discolouration kinetics values. No measurements could be performed at higher concentrations due to instrumental limitations related to the very high absorbances attained (>4 absorbance units).

2.2.3. Compounds 5a-d. Compounds 5a-d have a naphtho[1,2-b]pyran or a naphtho[2,1-b]pyran linked to a non-photochromic 13-oxoindeno[2,1-f]naphtho[1,2-b]pyran.⁴ Before UV irradiation they all show a small absorption band with a maximum between 489-503 nm (Abs: 0.20–0.23; $\varepsilon = 2000-2300 \text{ mol}^{-1} \text{ L cm}^{-1}$), which is responsible for their orange/red colourations. Upon irradiation of compounds 5a-c with UV light a new band appears as a shoulder between 430-438 nm that can be assigned to the opening of the naphtho[2,1-b]pyran ring (Table 1). From the position of these bands it is apparent that no enhancement in the extension of conjugation is achieved even with a conjugative bridge. The observed A_{eq} for these compounds (0.14-0.21) are lower than the colourabilities observed for the mono-photochromic 4a-c (0.19-0.25) and for Ref1 (0.27) (Fig. 3), although there is no apparent increase in the bleaching kinetics. The analysis of the fading kinetics of **5a-c** shows a good fit to

a tri-exponential model indicating that upon UV irradiation a more complex mixture is obtained.

Compound 5d, also already orange/red ($\lambda_{max} = 489 \text{ nm}$) coloured before UV-irradiation, associates a 2,2-diphenylnaphtho[1,2-b]pyran and the non-photochromic 2,2-diphenyl-13-oxoindeno[2,1-f]naphtho[1,2-b]pyran through a para substituted phenyl group. Upon irradiation with UV light this compound develops a stronger and wider band with a λ_{max} at 479 nm indicating the opening of the non-fused naphtho[1,2-b]pyran ring (Table 2). This bathochromic shift, relative to **Ref3** and the model compound **4d**, points to an increase of the π -conjugation. The usual dual kinetic of thermal bleaching of naphthopyrans, indicating the presence of TT and TC isomers, was observed. The similarity of the kinetic constants and amplitudes with the mono-photochromic model compound 4d and Ref3 indicates that the presence of the non-photochromic moiety has a negligible effect on the thermal stability of 5d.

2.2.4. Compounds 6a–d. Compounds 6a–c have two different photochromic units, a naphtho[2,1-*b*]pyran and a 13-methyl-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran, linked through PhOPh, Ph, and PhCH₂CH₂Ph bridges, respectively. Taken independently, upon irradiation with UV light, one residue (**Ref1**), generates an open form with a λ_{max} centered at 432 nm (A_{eq} =0.27) while the other (**Ref2**) generates an open form with two absorption maxima in the visible region: one at 530 nm (A_{eq} =1.3) and the other near 419 nm (A_{eq} =0.72) (Fig. 5). Moreover, the two photochromic units exhibit biexponential bleaching kinetics, although with quite different values in the initial fading rate: **Ref1** (6×10⁻² s⁻¹, 73%) fades initially about 20 times faster than **Ref2** (3×10⁻³ s⁻¹, 82%).

The covalent linkage of these two units yielded molecules that exhibit thermally reversible photochromic properties. As expected, due to the very different colourabilities of the associated units, the photochromic properties of the indeno-fused naphtho[1,2-*b*]pyran unit practically overlap those observed for the other naphtho[2,1-*b*]pyran and consequently, for the bi-photochromic compounds **6a–c**, it is very difficult to distinguish between their behaviour and those of



Figure 5. Absorption spectra of Ref1, Ref2, mixture Ref1+Ref2 and 6a after UV irradiation.

Ref2. In what it concerns the visible spectra of the open forms of bi-photochromic compounds **6a**–**c** only subtle differences are observed even when compared with a solution of the same concentration of an equimolar mixture of **Ref1** and **Ref2** (see Fig. 5).

However, colourabilities obtained at the lower λ_{max} (where the maximum contribution of the **Ref1** residue is expected) are higher than for **Ref2** alone and kinetic curves constants and amplitudes at this λ_{max} , show a good fit to a triexponential model with values in a range that may indicate that both pyran units are opened. The faster kinetic constant $(4 \times 10^{-2} - 7 \times 10^{-2} \text{ s}^{-1})$, representing 4–6% of the absorbance decay can be attributed to the TC isomer resulting from the opening of the naphtho[2,1-*b*]pyran (**Ref1**) while the second slower kinetic constant $(3 \times 10^{-3} - 5 \times 10^{-3} \text{ s}^{-1})$ representing 78–83% is probably due to the fading of the TC isomer resulting from the opening of the indeno[2,1-*f*]naphtho[1,2-*b*]pyran moiety.

Although the diphenyl ether bridge of series **a** (L=Ph-O-Ph) induced an expected small bathochromic shift in the visible spectra and some thermal instability of the open forms, it is apparent that the nature of the covalent bridge has no significant effect on the photochromic performances of the bi-naphthopyrans **6a–c**.

Compound **6d** is a bi-photochromic molecule associating two different naphthopyrans (**Ref2** and **Ref3**) with similar absorbances at the λ_{max} of the open forms (Table 4), linked through a shared *p*-phenyl substituted ring. Taken independently the two photochromes exhibit quite different fading kinetics although with similar amplitudes: the first fading rate of **Ref2** ($3 \times 10^{-3} \text{ s}^{-1}$, 82%), is about five times faster than the first fading rate of **Ref3** ($6 \times 10^{-4} \text{ s}^{-1}$, 76%). When solutions of each compound were submitted to UV irradiation, under identical experimental conditions, similar absorbance values were attained at the photostationary state: **Ref3**: $A_{eq} = 1.5$ (470 nm); **Ref2**: $A_{eq} = 1.3$ (533 nm). Compound **6d** led to the formation of a single wide absorption band with a maximum centred at 530 nm and higher colourability ($A_{eq} = 2.0$), suggesting the opening of both photochromic entities (Fig. 6).



Figure 6. Absorption spectra of Ref2, Ref3, mixture Ref2+Ref3 and 6d after UV irradiation.



Figure 7. Time evolution of the absorption spectrum of the opened form of compound 6d.

For this compound, fading kinetics were measured at 472 nm (major contribution of the naphtho[1,2-*b*]pyran residue), 530 nm (major contribution of the indeno-fused naphtho[1,2-*b*]pyran residue) and 620 nm (sole absorption contribution from the indeno-fused naphtho[1,2-*b*]pyran residue) and although the same values for the constants were found (Table 4), amplitudes varied in an expected way: the amplitude of the kinetic increased along with the increase of the contribution of the naphthopyran residue that is responsible for it.

Spectral evolution of the UV–vis spectrum of compound **6d** was also recorded during the thermal bleaching of solutions (Fig. 7). Clearly, it can be observed a gradual displacement with time, of the λ_{max} toward shorter wavelengths until λ_{max} of **Ref3** (the slower photochromic entity) was attained. Indeed, photochromic properties of **6d** can be considered as the superposition of the properties of the two naphthopyran residues taken separately.

A final comparison was made between compound **6d** and an equimolar mixture of **Ref2** and **Ref3** of the same concentration $(1 \times 10^{-4} \text{ M})$. The absorption spectrum of the open form of **6d** shows a $\lambda_{max} = 530 \text{ nm}$ while the mixture exhibits a $\lambda_{max} = 494 \text{ nm}$. This difference in the λ_{max} (+36 nm) suggests that the phenyl spacer allows some conjugation between the OF of the two photochromic entities, although a completely planar structure is probably not obtained.

Comparison of the fading kinetics observed for compound **6d** and an equimolar mixture of **Ref2** and **Ref3** (Fig. 8) revealed that **6d** constitutes a system that bleaches faster. This suggests that the opened naphthopyran may act as an electron donor substituent.

3. Conclusion

New bi-photochromic molecules, containing two identical or two distinct diphenylnaphthopyran units, were obtained by generally applicable methods. The strategy involved the linkage of one of the geminal aryl aromatic substituents, using covalent bridges, namely *p*-Ph-, *p*-PhOPh- and



Figure 8. Colour bleaching of a mixture of Ref2+Ref3 and 6d.

p-PhCH₂CH₂Ph–. All compounds exhibited photochromic behaviour in toluene solutions at room temperature. Compared to the individual photochromic components and to model monophotochromes it was observed that the nature of the bridge has a small effect on the photochromic properties of each system.

Under continuous near UV-vis irradiation the two naphthopyran units of the bi-photochromic molecules **3a-d** and **6a-d**, were stimulated independently leading to open forms with higher colourabilities but without affecting the individual bleaching kinetics.

Considering the absorbance spectra of the open forms of the bi-photochromic molecules no additional extension of the π -conjugation was observed for 3,3-diphenylnaphtho-[2,1-*b*]pyran derivatives while for 2,2-diphenylnaphtho-[1,2-*b*]naphthopyran derivatives (**3d** and **6d**) it was evident a bathochromic shift of the λ_{max} , suggesting that for these last derivatives, under UV irradiation, structures with a better global planarity are obtained.

4. Experimental

4.1. Spectrokinetic studies under continuous irradiation

For measurements of λ_{max} , A_{eq} and k_{Δ} under continuous UV-vis irradiation, 1×10^{-4} M toluene solutions were used. 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-vis 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 a fiber-optic system (77654 Oriel Instruments). A 40 W m⁻² light flux, measured with a Goldilux Photometer with a UV-A probe, was used. A thermostated (20 °C) 10 mm quartz cell, containing the sample solution (3.5 ml), equipped with magnetic stirring was used. In a preliminary experiment, the visible absorption spectrum of the closed form 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 with the time was monitored. The thermal bleaching rate constants, k_{Δ} , were calculated fitting the absorbance curve obtained in the dark, at 20 °C, to a multi exponential model.

4.2. General remarks

¹H and ¹³C spectra were recorded for CDCl₃ solutions on a Bruker Avance 400 MHz instrument. IR spectra were obtained on a Perkin-Elmer FTIR 1600 spectrometer using KBr disks (wavenumbers in cm⁻¹). Electronic impact mass spectra were measured on a AutoSpecE spectrometer. Melting points (°C) measured at a Büchi 535 apparatus are uncorrected. The melting points of photochromic naphthopyrans **6a–d** were not determined because thermochromism was observed at high temperatures. Column chromatography (CC) was performed on silica gel 60 (70–230 mesh). THF was pre-dried under sodium/benzophenone and distilled before use. All new compounds were determined to be >95% pure by ¹H NMR spectroscopy.

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

n-Buthyllithium in hexanes (7.5 ml, 12 mmol) was added slowly with a syringe to a cold (-10 °C) stirred solution of trimethylsilylacetylene (1.7 ml, 12 mmol) in anhydrous THF (50 ml). The cold solution was stirred 1 h and then a solution of the diketone **1a–c** (4 mmol) in anhydrous THF was added and the mixture stirred at room temperature for 12 h. The reaction mixture was then cooled to 0 °C and a solution of KOH (0.84 g) in MeOH (10 ml) was added in a single portion. After stirring at room temperature for 30 min, the reaction mixture was poured into 50 ml of water and acidified to pH~7 with glacial acetic acid. The organic layer was separated and the aqueous layer extracted with ethyl acetate (3×50 ml). The combined organic phases were washed with water (2×50 ml) and dried (Na₂SO₄). Removal of the solvent gave diols **2a–c**, which were sufficiently pure for subsequent use.

4.3.1. 4,4'-Bis(1-hydroxy-1-phenyl-prop-2-yn-1-yl) diphenyl ether 2a. Light yellow oil. Yield 93%. IR: 3428, 3284, 2113, 1596, 1498, 1240; ¹H NMR: 7.61 (m, 4H), 7.54 (m, 4H), 7.40–7.22 (m, 6H), 6.93 (m, 4H), 2.97 (large s, 2H), 2.87 (s, 2H); MS: *m/z* (%): 430 (100), 413 (15), 353 (50), 207 (24), 131 (12), 105 (17), 77 (17).

4.3.2. 1,4-Bis(1-hydroxy-1-phenyl-prop-2-yn-1-yl)benzene 2b. Light yellow solid. Yield: 91%. Mp 143–145. IR: 3426, 3286, 2115, 1486, 1448, 1166; ¹H NMR: 7.59 (m, 4H), 7.57 (s, 4H), 7.32 (m, 4H), 7.27 (m, 2H), 2.90 (large s, 2H), 2.86 (s, 2H); MS: *m/z* (%): 338 (100), 321 (32), 261 (70), 207 (24), 131 (55), 105 (60), 77 (17).

4.3.3. 4', 4''-Bis(1-hydroxy-1-phenyl-prop-2-yn-1-yl)-1,2diphenylethane 2c. Light yellow oil. Yield: 97%. IR: 3421, 3288, 2956, 2115, 1448, 1178; ¹H NMR: 7.59 (d, *J*=7.2 Hz, 4H), 7.49 (d, *J*=8.2 Hz, 4H), 7.33 (dd, *J*=7.2 Hz, 4H), 7.27 (dd, *J*=7.2 Hz, 2H), 7.14 (d, *J*=8.2 Hz, 4H), 2.86 (m, 8H); MS: m/z (%): 442 (30), 424 (7), 297 (20), 221 (60), 204 (55), 105 (100).

4.4. General procedure for the reaction of 2-naphthol with diols 2a-c

A solution of diol **2a–c** (4.0 mmol), 2-naphthol (0.504 g, 3.5 mmol), PPTS (10 mg), CH(OMe)₃ (0.8 ml, 8 mmol) and 1,2-dichloroethane (50 ml) was refluxed for 2 h under nitrogen. Solvent evaporation gave a brown oil, which was purified by CC (3–15% ethyl acetate/hexane). Two compounds were obtained: bi-naphthopyrans **3a–c** (fraction 1 minor product) and naphthopyrans **4a–c** (fraction 2, major product). The following compounds were obtained using this protocol.

4.4.1. From 2-naphthol and diol 2a: 4,4'-bis[3-phenyl-3H-naphtho[2,1-b]pyran-3-yl]diphenyl ether 3a. White solid. Yield 16%. Mp 99-101. IR: 3056, 2923, 1590, 1496, 1240; ¹H NMR: 7.94 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.45 (m, 6H), 7.39 (m, 4H), 7.33–7.27 (m, 8H), 7.26–7.22 (m, 2H), 7.17 (d, J=8.8 Hz, 2H), 6.90 (m, 4H), 6.22 (d, J=10 Hz, 2H); ¹³C NMR: 156.3, 150.4, 144.8, 139.7, 129.8, 129.3, 128.9, 128.6, 128.5, 128.3, 128.1, 127.6, 126.9, 126.6, 125.9, 123.6, 121.3, 119.5, 118.3, 113.9, 82.2; MS: m/z (%): 682 (5), 608 (4), 570 (5), 460 (5), 391 (7), 307 (35), 154 (100), 137 (68). 4-[3-Phenyl-3H-naphtho[2,1-b]pyran-3-yl]-4'-(1-hydroxy-1-phenyl-prop-2-yn-1-yl)diphenyl ether 4a. Yellow oil. Yield 42%. IR: 3444, 3280, 3058, 1590, 1494, 1238; ¹H NMR: 7.95 (d, J=8.4 Hz, 1H), 7.71 (d, J=8.0 Hz, 1H), 7.66 (d, J=8.8 Hz, 1H), 7.59 (m, 2H), 7.55–7.40 (m, 7H), 7.37–7.22 (m, 8H), 7.18 (d, J = 9.0 Hz, 1H), 6.92 (m, 4H), 6.24 (d, J = 10 Hz, 1H), 2.87 (s, 1H), 2.77 (s, 1H); ¹³C NMR: 156.6, 156.4, 150.4, 144.8, 144.3, 139.8, 139.4, 129.9 (two signals), 128.6, 128.5, 128.3, 128.1, 127.9, 127.62, 127.58, 127.54, 126.9, 126.6, 125.9, 123.6, 121.3, 119.5, 118.6, 118.3, 113.9, 86.3, 82.2, 75.5, 73.9; MS: m/z (%): 556 (100), 530 (5), 479 (40), 257 (40).

4.4.2. From 2-naphthol and diol 2b: 1,4-bis[3-phenyl-3Hnaphtho[2,1-b]pyran-3-yl]benzene 3b. White solid. Yield 20%. Mp > 250. IR: 3060, 2921, 1627, 1583, 1213; ¹H NMR: 7.97 (d, J=8.4 Hz, 2H), 7.72 (d, J=8.4 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.58–7.40 (m, 10H), 7.38–7.22 (m, 10H), 7.20 (d, J = 8.8 Hz, 2H), 6.26 (d, J = 10 Hz, 2H); ¹³C NMR: 150.5, 144.6, 144.2, 129.81, 129.77, 129.31, 128.5, 128.2, 128.0, 127.5, 127.0, 126.8, 126.6, 123.6, 121.3, 119.4, 118.3, 113.9, 82.4; MS: m/z (%): 590 (35), 478 (70), 447 (50), 391 (60), 257 (100), 154 (95), 136 (80). 3-Phenyl-3-[p-(1-hydroxy-1-phenyl-prop-2-yn-1-yl)phenyl]-3Hnaphtho[2,1-b]pyran 4b. White solid. Yield 43%. Mp 173-174. IR: 3548, 3438, 3272, 3056, 1631, 1587, 1444, 1216; ¹H NMR: 7.94 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8 Hz, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.59 (m, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.50–7.40 (m, 5H), 7.37–7.20 (m, 8H), 7.18 (d, J =8.8 Hz, 1H), 6.24 (d, J = 10 Hz, 1H), 2.86 (s, 1H), 2.77 (s, 1H); ¹³C NMR: 150.4, 144.54 (two signals), 144.0, 143.5, 129.9, 129.7, 129.3, 128.5, 128.3, 128.1, 127.9, 127.6, 127.4, 127.0, 126.9, 126.6, 125.9, 125.8, 123.6, 121.3, 119.5, 118.3, 113.9, 86.3, 82.3, 75.5, 74.1; MS: m/z (%): 464 (100), 387 (45), 333 (20), 257 (70), 131 (12), 105 (16), 77 (13).

4.4.3. From 2-naphthol and diol 2c: 4',4"-bis[3-phenyl-3*H*-naphtho[2,1-*b*]pyran-3-yl]-1,2-diphenylethane 3c.

White solid. Yield 22%. Mp 204-205. IR: 3056, 3023, 2921, 1629, 1587, 1511, 1446, 1222; ¹H NMR: 7.95 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.5– 7.4 (m, 6H), 7.36 (d, J = 7.8 Hz, 4H), 7.30 (m, 8H), 7.25 (m, 2H), 7.19 (d, J = 8.8 Hz, 2H), 7.11 (m, 4H), 6.24 (dd, J =1.2 Hz, 9.9 Hz, 2H), 2.84 (s, 4H); ¹³C NMR: 150.5, 144.9, 142.4, 141.1, 129.8, 129.3, 128.5, 128.1, 127.8, 127.5, 127.1 (two signals), 126.9 (two signals), 126.6, 123.5, 121.3, 119.4, 118.4, 114.0, 82.4, 37.3; MS: m/z (%): 694 (5), 582 (20), 505 (10), 446 (15), 318 (35), 257 (22), 227 (55), 131 (34), 119 (50), 91 (100). 4'-[3-Phenyl-3H-naphtho[2,1b]pyran-3-yl]-4"-(1-hydroxy-1-phenyl-prop-2-yn-1-yl)-1,2-diphenylethane 4c. Yellow oil. Yield 38%. IR: 3419, 3284, 3056, 1648, 1589, 1446, 1243; ¹H NMR: 7.93 (d, *J*= 8.5 Hz, 1H), 7.68 (d, J=8.0 Hz, 1H), 7.63 (d, J=8.0 Hz, 1H), 7.58 (m, 2H), 7.50–7.40 (m, 5H), 7.37 (d, J=8.3 Hz, 2H), 7.32–7.15 (m, 9H), 7.12 (m, 4H), 6.24 (d, J=10 Hz, 1H), 2.86 (large s, 1H), 2.82 (m, 5H); ¹³C NMR: 150.5, 144.9, 144.4, 142.5, 142.1, 141.4, 141.0, 129.7, 129.2, 128.5, 128.3, 128.1, 127.8, 127.4, 127.1, 126.9, 126.6, 126.0, 125.9, 123.5, 121.3, 119.4, 118.3, 114.0, 86.4, 82.5, 75.5, 74.0, 37.3, 37.2; MS: m/z (%): 568 (50), 551 (10), 542 (17), 491 (20), 345 (25), 257 (50), 105 (32), 91 (100).

4.4.4. Procedure for the reaction of 1-naphthol with diol **2b.** A solution of diol **2b** (4.0 mmol), 1-naphthol (0.504 g, 3.5 mmol), PPTS (10 mg), CH(OMe)₃ (0.8 mL, 8 mmol) and 1,2-dichloroethane (50 ml) was refluxed for 2 h under nitrogen. Solvent evaporation gave a brown oil, which was purified by CC (3-15% ethyl acetate/hexane). Two compounds were isolated. 1,4-Bis[2-phenyl-2Hnaphtho[1,2-b]pyran-2-yl]benzene 3d. Pale pink solid. Yield 8%. IR: 3052, 1644, 1617, 1446, 1394, 1371, 1267, 1097; ¹H NMR: 8.31 (dd, J=7.5, 1.8 Hz, 2H), 7.70 (dd, J= 7.2, 1.8 Hz, 2H), 7.50-7.38 (m, 12H), 7.35-18 (m, 8H), 7.13 (d, J=8.3 Hz, 2H), 6.68 (d, J=9.7 Hz, 2H), 6.12 (d, J=9.7 Hz, 2H); ¹³C NMR: 147.7, 144.9, 144.4, 134.6, 128.1, 127.6, 127.5, 127.1, 126.8, 126.64, 126.59, 126.3, 125.5, 124.6, 123.7, 122.0, 120.4, 115.3, 83.0; MS: m/z (%): 590 (100), 513 (10), 447 (10), 436 (10), 322 (16), 257 (41), 185 (40), 105 (24), 77 (27). 2-Phenyl-2-[p-(1-hydroxy-1phenyl-prop-2-yn-1-yl)]phenyl-2H-naphtho[1,2-b]pyran 4d. Yellow oil. Yield 32%. IR: 3415, 3282, 3027, 2923, 1446, 1371; ¹H NMR: 8.31 (d, J=8.1 Hz, 1H), 7.73 (d, J= 8.6 Hz, 1H), 7.60–7.38 (m, 12H), 7.30–7.18 (m, 5H), 7.11 (d, J=8.3 Hz, 1H), 6.68 (d, J=9.7 Hz, 1H), 6.12 (d, J=10 Hz, 1H), 2.85 (large s, 1H), 2.80 (m, 1H); ¹³C NMR: 147.6, 144.9, 144.8, 144.0, 143.5, 134.6, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 126.8, 126.3, 125.90, 125.88, 125.84, 125.82, 125.6, 124.5, 123.8, 121.9, 120.5, 115.3, 86.3, 82.8, 75.5, 74.1; MS: m/z (%): 464 (100), 446 (70), 387 (37), 333 (27), 257 (52), 105 (24), 77 (19).

4.5. General procedure for the synthesis of bi-naphthopyrans 5a-d

A solution of compounds **4a–d** (1.0 mmol), 5-hydroxy-7*H*benzo[*c*]fluoren-7-one (0.246 g, 1.1 mmol), PPTS (10 mg), CH(OMe)₃ (0.2 mL, 2 mmol) and 1,2-dichloroethane (50 ml) was refluxed for 2 h under nitrogen. Solvent evaporation gave a red oil, which was purified by CC (3– 10% ethyl acetate/hexane). Recrystallization from hexane/ CHCl₃ gave crystalline materials. 4.5.1. 4-[3-Phenyl-3*H*-naphtho[2,1-*b*]pyran-3-yl]-4'-[13oxo-3-phenyl-indeno[2,1-f]naphtho[1,2-b]pyran-3-yl] diphenyl ether 5a. Red crystals. Yield 77%. Mp 150 d. IR: 3058, 2954, 1702, 1598, 1496, 1240, 1170; ¹H NMR: 8.35 (m, 2H), 7.94 (d, J=8.4 Hz, 1H), 7.89 (d, J=9.9 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.64 (d, J=8.8 Hz, 1H), 7.55 (m, 3H), 7.50–7.35 (m, 10H), 7.32– 7.18 (m, 9H), 7.17 (d, J=8.8 Hz, 1H), 6.90 (m, 4H), 6.32 (d, J=9.9 Hz, 1H), 6.22 (d, J=9.9 Hz, 1H); ¹³C NMR: 195.9, 156.5, 156.2, 150.4, 149.1, 144.9, 144.8, 144.6, 139.8, 139.4, 135.5, 134.5, 134.4, 129.84, 129.8, 129.7, 129.32, 129.29, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 126.9, 126.8, 126.6, 126.2, 124.7, 123.7, 123.6, 123.5, 122.3, 121.3, 119.6, 119.5, 118.44, 118.38, 118.3, 113.9, 113.3, 105.7, 83.3, 82.2; MS (FAB): m/z (%): 785 ([M+1]⁺, 7), 784 (M⁺, 6), 707 (2), 659 (2), 391 (14), 338 (25), 154 (100), 136 (74); HRMS: $[C_{57}H_{36}O_4]^+$, found 784.2628, requires 784.2614.

4.5.2. 13-Oxo-3-phenyl-3-[p-(3-phenyl-3H-naphtho[2,1b]pyran-3-yl)]phenyl-indeno[2,1-f]naphtho[1,2-b]pyran 5b. Red crystals. Yield 67%. Mp 135-138 d. IR: 3058, 2923, 1702, 1602, 1461, 1369; ¹H NMR: 8.36 (m, 2H), 7.93 (d, J=8.4 Hz, 1H), 7.87 (d, J=10 Hz, 1H), 7.86 (d, J=7.6 Hz, 1H), 7.69 (d, J=7.9 Hz, 1H), 7.63 (d, J=8.8 Hz, 1H), 7.55 (m, 3H), 7.50–7.40 (m, 10H), 7.30–7.18 (m, 9H), 7.16 (d, J=8.7 Hz, 1H), 6.32 (d, J=9.9 Hz, 1H), 6.23 (d, J=9.9 Hz, 1H); ¹³C NMR: 195.7 (two signals), 150.4, 149.1, 144.8 (two signals), 144.5 (two signals), 144.4 (two signals), 144.0, 135.5, 134.5 (two signals), 134.3 (two signals), 129.8 (two signals), 129.7 (two signals), 129.3, 128.5, 128.4, 128.2, 128.1, 127.8 (two signals), 127.7, 127.6, 127.5, 127.4, 126.94, 126.9 (two signals), 126.64, 126.6 (two signals), 126.2 (two signals), 124.7, 123.6, (two signals), 123.5 (two signals), 122.3 (two signals), 121.24, 122.19, 119.6 (two signals), 119.5, 118.3 (two signals), 113.8, 113.3 (two signals), 83.4 (two signals), 82.3; MS: m/z (%): 692 (5), 583 (6), 555 (12), 527 (5), 391 (90), 149 (100); HRMS: $[C_{51}H_{32}O_3]^+$, found 692.2363, requires 692.2351.

4.5.3. 4'-[3-Phenyl-3*H*-naphtho[2,1-*b*]pyran-3-yl]-4"-[13-oxo-3-phenyl-indeno[2,1-f]naphtho[1,2-b]pyran-3yl]-1,2-diphenylethane 5c. Red crystals. Yield 60%. Mp 108–111 d. IR: 3054, 2921, 1702, 1600, 1455, 1367; ¹H NMR: 8.38 (m, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.87 (m, 2H), 7.70 (d, J=8.2 Hz, 1H), 7.64 (d, J=8.8 Hz, 1H), 7.60-7.14 (m, 27H), 6.33 (m, 1H), 6.24 (d, J=9.9 Hz, 1H), 2.84 (s, 4H); ¹³C NMR: 195.9, 158.6, 150.5, 149.2, 144.9 (two signals), 144.7, 142.5, 142.2, 141.3, 141.0, 135.4, 134.5, 134.4, 130.0, 129.7, 129.3 (two signals), 128.5, 128.2 (three signals), 128.0, 127.9 (two signals), 127.8, 127.6, 127.5, 127.4, 127.1, 127.0, 126.9 (two signals), 126.8, 126.6, 126.5, 126.0, 124.7, 123.6, 123.5, 122.3, 121.3, 119.5, 119.4, 118.3, 114.0, 113.4, 83.5, 82.4, 37.30, 37.26; MS (FAB) m/z (%): 797 ($[M+1]^+$, 35), 796 (M^+ , 33), 663 (35), 641 (65), 608 (45), 580 (72), 555 (100), 527 (44), 419 (53); HRMS: $[C_{59}H_{40}O_3]^+$, found 796.3011, requires 796.2977.

4.5.4. 13-Oxo-3-phenyl-3-[*p*-(**2-phenyl-2***H***-naphtho**[**1**,2-*b*]**pyran-2-yl**]**]phenyl-indeno**[**2**,1-*f*]**naphtho**[**1**,2-*b*]**pyran 5d.** Red crystals. Yield 69%. Mp 138–143 d. IR: 3052, 2921, 1702, 1579, 1461, 1400, 1367; ¹H NMR: 8.36–8.29 (m, 4H), 7.86 (m, 1H), 7.80 (m, 2H), 7.68 (m, 1H), 7.60–7.32

(m, 15H), 7.32–7.10 (m, 6H), 6.68 (m, 1H), 6.32 (d, J=10 Hz, 1H), 6.14 (d, J=9.8 Hz, 1H); ¹³C NMR: 195.8, 149.1, 147.6, 144.9, 144.7, 144.3, 143.9, 135.5, 134.6, 134.5, 134.4, 129.7, 129.3, 128.2, 128.1, 128.0, 127.81, 127.75, 127.61, 127.56, 127.5, 127.0, 126.9, 126.8, 126.70, 126.66, 126.5, 126.4, 126.3, 126.2, 125.6, 124.7, 124.6, 124.5, 123.8, 123.6, 123.5, 122.3, 122.0, 120.5, 115.3, 113.2, 83.4, 83.0; HRMS: $[C_{51}H_{32}O_3]^+$, found 692.2367, requires 692.2351.

4.6. General procedure for the synthesis of photochromic naphthopyrans 6a–d

A solution of CH₃MgI in dry Et₂O (1 ml, 1 mmol) was added slowly to a cold solution (0 °C) of naphthopyrans **5a–d** (0.25 mmol) in THF (10 ml). After stirring at room temperature for 1 h, the solution was quenched in aqueous satd NH₄Cl, extracted with Et₂O (3×40 ml), dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by CC (3-10% ethyl acetate/light petroleum). Recrystallization from hexane/CHCl₃ gave a crystalline material.

4.6.1. 4-[3-Phenyl-3*H*-naphtho[2,1-*b*]pyran-3-yl]-4'-[13hydroxy-13-methyl-3-phenyl-indeno[2,1-f]naphtho[1,2**b**]pyran-3-yl]diphenyl ether 6a. Pale red crystals. Yield 79%. IR: 3355, 3055, 2956, 1596, 1495, 1235; ¹H NMR: 8.51 (d, J=8.5 Hz, 1H), 8.42 (d, J=8.3 Hz, 1H), 8.05 (d, J=7.7 Hz, 1H), 7.93 (d, J=8.4 Hz, 1H), 7.70 (d, J=8.1 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.60–7.15 (m, 24H), 6.93-6.86 (m, 4H), 6.25-6.18 (m, 2H), 2.04 (s, OH), 1.78 (m, 3H, CH₃); ¹³C NMR: 158.3, 156.6, 156.3, 156.1, 151.0, 150.4, 148.6, 145.3, 144.8, 144.6, 143.8, 140.2, 139.82, 139.75, 139.5, 139.3, 129.84, 129.79, 129.3, 128.9, 128.6, 128.5, 128.4, 128.22, 128.16, 128.1, 127.8, 127.7, 127.6, 127.5, 127.3, 126.9, 126.65, 126.63, 126.2, 125.4, 123.9, 123.6, 123.2, 122.4, 122.1, 121.3, 120.6, 119.5, 118.5, 118.4, 118.3, 118.2, 113.9, 113.0, 82.74, 82.69, 82.2, 80.67, 80.64, 26.6; HRMS: $[C_{58}H_{40}O_4]^+$, found 800.2938, requires 800.2927.

4.6.2. 13-Hydroxy-13-methyl-3-phenyl-3-[p-(3-phenyl-3H-naphtho[2,1-b]pyran-3-yl)]phenyl-indeno[2,1-f] naphtho[1,2-b]pvran 6b. Pale red crystals. Yield 75%. IR: 3388, 3264, 2923, 1633, 1365; ¹H NMR: 8.52 (m, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.06 (m, 1H), 7.92 (m, 1H), 7.72-7.10(m, 26H), 6.24 (d, J=9.9 Hz, 1H), 6.23 (m, 1H), 2.00 (s, 1H, OH), 1.7 (m, 3H, CH₃); ¹³C NMR: 151.0 (two signals), 150.4 (two signals), 148.6, 145.6, 144.6, 144.4 (two signals), 144.3 (two signals), 144.1, 144.0 (two signals), 143.9, 143.8, 139.5, 129.8 (two signals), 129.3, 128.9, 128.5, 128.2, 128.1, 128.05, 128.01, 127.7, 127.5 (two signals), 127.3, 127.0 (two signals), 126.9 (two signals), 126.8 (two signals), 126.7, 126.6, 126.5, 126.1, 125.4, 123.9, 123.6, 123.3, 122.4, 122.0, 121.3, 120.6, 120.5, 119.4, 119.3 (two signals), 118.31, 118.27, 113.9, 113.8, 113.0, 112.8, 82.8, 82.4 (two signals), 80.6 (two signals), 26.4 (two signals); MS (FAB): *m*/*z* (%): 708 (1), 691 (1), 663 (1), 53 (2), 555 (4), 460 (5), 307 (35), 154 (100), 137 (67); HRMS: $[C_{52}H_{36}O_3]^+$, found 708.2684, requires 708.2664.

4.6.3. 4'-[3-Phenyl-3*H*-naphtho[2,1-*b*]pyran-3-yl]-4"-[13-hydroxy-13-methyl-3-phenyl-indeno[2,1-*f*]naphtho[1, **2-***b***]pyran-3-yl]-1,2-diphenylethane 6c.** Pale red crystals. Yield 70%. IR: 3330, 3023, 2924, 1633, 1366; ¹H NMR: 8.51 (d, J=8.3 Hz, 1H), 8.44 (d, J=8.3 Hz, 1H), 8.06 (d, J=7.7 Hz, 1H), 7.92 (m, 1H), 7.69 (d, J=8.1 Hz, 1H), 7.63 (d, J=7.5 Hz, 1H), 7.60–7.00 (m, 28H), 6.27–6.18 (m, 2H), 2.8 (m, 4H), 2.05 (s, OH), 1.78 (m, 3H, CH₃); ¹³C NMR: 151.0, 150.5, 148.7, 145.5, 144.9, 144.7, 143.9, 143.0, 142.5, 141.2, 141.1, 139.6, 129.8, 129.3, 128.9, 128.5, 128.2, 128.11, 128.05, 128.0, 127.8, 127.6, 127.44, 127.36, 127.3, 127.04, 127.01, 126.8, 126.7, 126.6, 126.12, 126.06, 125.43, 125.36, 123.9, 123.6, 123.3, 122.4, 122.1, 121.3, 120.6, 119.4, 118.4, 114.0, 113.0, 82.9, 82.4, 80.7, 37.32, 37.31, 26.4; HRMS: $[C_{60}H_{44}O_3]^+$, found 812.3273, requires 812.3290.

4.6.4. 13-Hydroxy-13-methyl-3-phenyl-3-[p-(2-phenyl-2H-naphtho[1,2-b]pyran-2-yl)]phenyl-indeno[2,1-f] naphtho[1,2-b]pyran 6d. Pale red crystals. Yield 73%. IR: 3371, 3286, 3053, 2923, 1642, 1393, 1367; ¹H NMR: 8.51 (m, 1H), 8.42 (m, J = 8.4 Hz, 1H), 8.31 (m, 1H), 8.05 (m, 1H), 7.68 (m, 1H), 7.60–7.32 (m, 15H), 7.32–7.18 (m, 8H), 7.12 (m, 1H), 6.68 (m, 1H), 6.23 (m, 1H), 6.16 (d, J=9.7, 0.5 Hz), 6.13 (d, J=9.7, 0.5 Hz), 2.03 (s, 1H, OH), 1.80 (m, 3H, CH₃); ¹³C NMR: 151.01, 150.95, 148.6, 147.65, 147.63, 145.05, 144.96, 144.9, 144.8, 144.6, 144.5, 144.3, 143.9, 143.8, 139.5, 134.6, 129.8, 128.9, 128.2, 128.1, 128.0, 127.7, 127.6, 127.50, 127.47, 127.3, 127.1, 127.0, 126.8, 126.74, 126.71, 126.64, 126.60, 126.57, 126.3, 126.1, 125.8 (two signals) 125.40, 125.36, 124.5 (two signals), 123.9, 123.3, 123.1, 123.0, 122.4, 122.1, 122.0, 120.6, 120.4 (two signals), 115.3, 115.2, 113.0, 112.9, 112.8 (two signals), 83.0 (two signals), 80.6 (two signals), 26.4, 26.3; HRMS: $[C_{52}H_{36}O_3]^+$, found 708.2652, requires 708.2664.

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