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Synthesis and unexpected photochemical behaviour of biphotochromic systems involving spirooxazines and naphthopyrans linked by an ethylenic bridge

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Abstract—Using the Wittig reaction, six new biphotochromic compounds have been prepared by the coupling of conveniently functionalised spiro[indoline–naphthoxazines] and naphthopyrans. Compared to molecules taken individually, unusual photochromic behaviour has been detected with compounds for which a double bond of *Z*-configuration links both entities by the 5 or 5′ positions of the naphthalenic parts. Indeed, in this case the thermally stable uncoloured and coloured forms (bistable system) can be photochemically converted acting as photochemical switches.

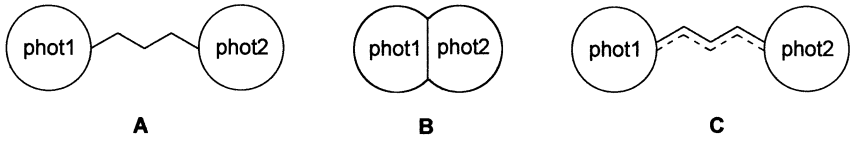
1. Introduction

The light induced colour change of organic compounds, i.e. photochromism, has been subjected to extensive investigation, due to a wide range of applications.[1–3] Among the different challenges in this field, the design of molecules in which two photochromic entities are covalently linked is especially attractive. This kind of compounds, named 'biphotochromics' by H. Dürr,[1] are a subject of interest for a number of research teams, resulting in the increase of publications and patents during the last few years. Many families of organic photochromic compounds are involved: spiropyrans,[4–9] spirooxazines,[10–13] dihydroindolizines,[13–16] Schiff bases,[14] dihydroazulenes,[17–18] diarylnaphthopyrans,[12,19] dithienylethenes.[18] The objectives of these different studies are diverse and depend on the structure of the involved photochromic units but also on the kind of linkage.

With biphotochromic compounds linked by a non-conjugated chain (A, Scheme 1), the main goals are to bring structural modifications able to favour the auto-assembling of the coloured photoinduced forms. On the other hand, when the spacer hold complexing ability like polyethers,[11] polyamides,[4–6] or calix[4]arenes,[16] the photomodulation of the complexation, and the variation of the photochromic properties by supramolecular effects are possible.

The objectives are different for annellated biphotochromics (B, Scheme 1) including usually a shared aromatic ring[10,12,13] and for biphotochromic molecules for which the spacer is a conjugated chain (C).

Contrary to type A compounds, photochromic entities are not independent here and their simultaneous photoexcitation becomes problematic. Nevertheless, when this specificity occurs, unusual spectrokinetic properties of the coloured



Scheme 1.

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species can be observed.[13] On the other hand, providing that a selective photoexcitation was possible, biphotochromics of B and C types can be considered as multimode switching systems.[18]

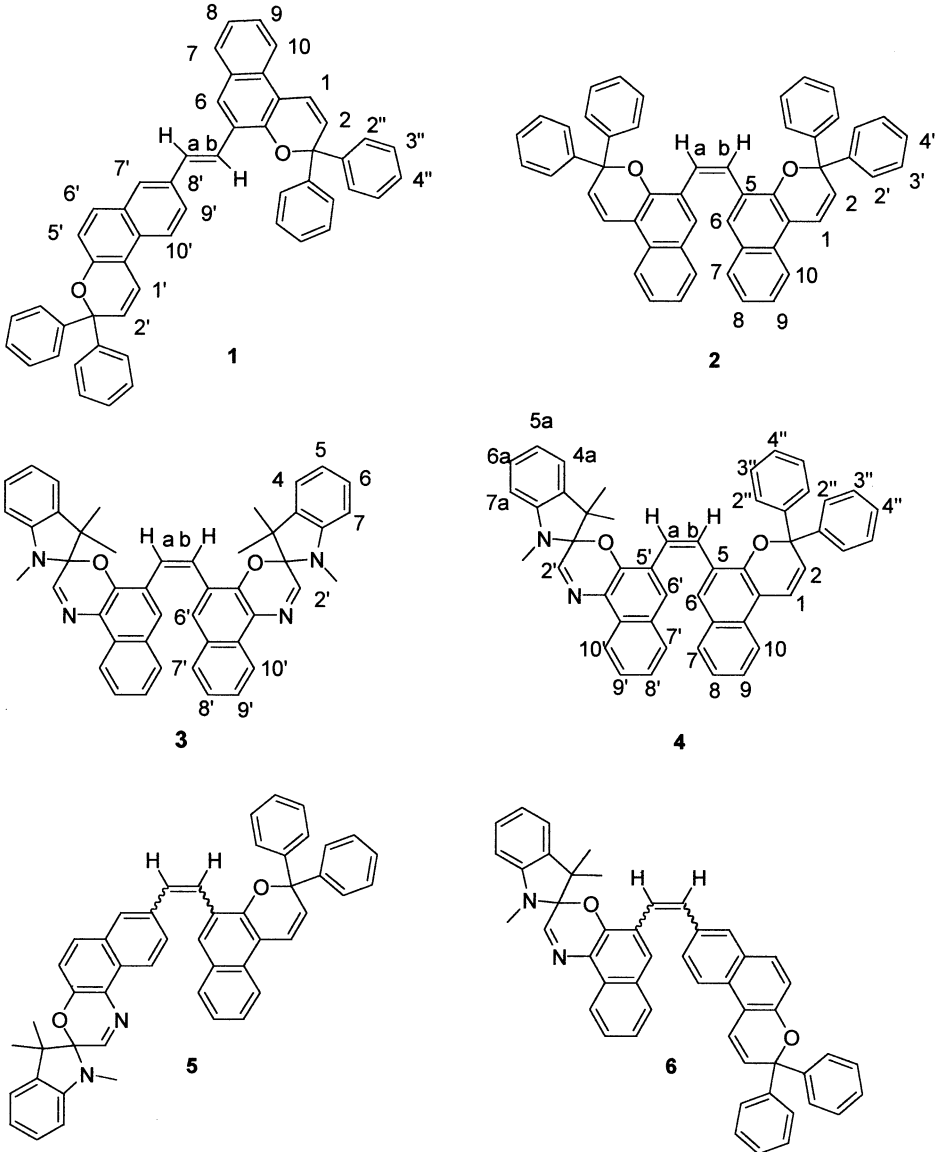
In the frame of our studies related to photochromic spirooxazines and diarylnaphthopyrans[20–24] we have decided to study biphotochromics including these two families of compounds. Our work was especially devoted to type C molecules (Scheme 1) in which the spacer is an ethylenic bond, the aim being to prepare and to make a preliminary study of the photochromic behaviour of compounds **1**–**6**.

2. Results and discussion

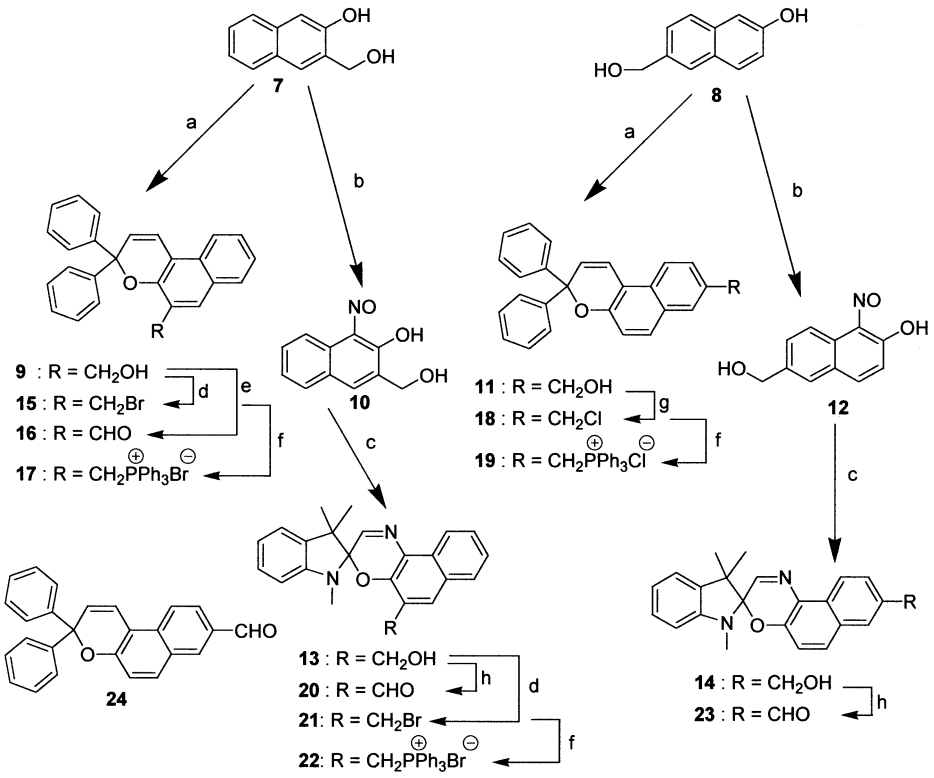
2.1. Synthesis

To prepare biphotochromic compounds **1**–**6** (Scheme 2), we have chosen the Wittig reaction as simple and efficient method to build the carbon–carbon double bond acting as the linking arm between the two photochromic units. The success of this aim was dependent on the possible functionalisation of spiro[indoline–naphthoxazines] and naphthopyrans, a work we developed in our laboratory for several years[20,25,26] and which has been extended in the present paper.

Carboxaldehydes and phosphonium salts (usual precursors for the Wittig reaction) might be a priori easily prepared from hydroxymethyl groups born by photochromic molecules. In both series (spirooxazines and naphthopyrans) these derivatives can be obtained from two main starting materials (Scheme 3): 3-hydroxymethyl-2-naphthol **7**[27] and 6-hydroxymethyl-2-naphthol **8**; to our knowledge this latest is not described in the literature, but can be afforded by the reduction of 6-hydroxy-2-naphthaldehyde[20]. Then the reaction of these naphthols (**7** and **8**) with 1,1-diphenylpropyn-1-ol[28] leads to hydroxymethylated naphthopyrans (**9** and **11**), while their nitrosation, followed by a classical[29]



Scheme 2.



Scheme 3. *Reagents and conditions*: (a) 1,1-diphenylpropyn-1-ol, CH_3CN, *p*-toluenesulphonic acid (cat.), rt: (b) $NaNO_2$, H_2SP_4, Pyridine, 0°C: (c) 2-methylene-1,3,3-trimethylindoline (Fischer base), EtOH or trichloroethylene, reflux: (d) Br_2/PPh_3, CH_2Cl_2, rt: (e) PCC, CH_2Cl_2, rt: (f) PPh_3, toluene, reflux: (g) $SoCl_2$, Et_2O, rt: (h) Dess–Martin periodinane, CH_2Cl_2, rt.

condensation with the Fischer base, allow the preparation of spirooxazines (**13** and **14**) bearing the same functional groups on the 5′ and 8′ position, respectively.

These reactions and the transformations of hydroxymethylated intermediates into the expected precursors are summarised on Scheme 3. Among the compounds included in this scheme, the spirooxazine **13** has been already mentioned in the literature[30] but not fully characterised. On the other hand, the synthesis of naphthopyrans **9**, **16**, **24**[20] and spirooxazine **20**[26] has been previously described by our laboratory.

Oxazine and naphthopyran precursors (aldehydes and phosphonium salts) have been used to perform Wittig reactions, leading to biphotochromic compounds **1–6** with satisfying yields (Table 1). Biphasic conditions (toluene/50% aqueous solution of NaOH), in which the phosphonium salt acts as phase transfer catalyst[31] have been applied. In the case of the preparation of compounds **1** and **4**, two different combinations for the starting materials have been used, both methods giving comparable yield. Structure of compounds **1–6** has been established by ^1H and ^{13}C NMR spectroscopies, mass spectrometry and elemental analysis. Molecular masses confirm without doubt the dimeric character of the compounds.

Moreover, characteristic signals in ^1H NMR spectra (like $C(CH_3)_2$:1.31–1.41 ppm, $N–CH_3$: 2.65–2.75 ppm, H-10′: 8.30–8.60 ppm for spirooxazine and H-2: 6.20–6.30 ppm for naphthopyrans) allow to identify unambiguously the nature of the involved photochromic units.

As expected for Wittig reactions, mixtures of *E* and *Z*

Table 1. Preparation details of biphotochromics **1–6**

Compound	Precusors		Isomer ratio[a]	Yield (%) (isolated isomer)
	Phosphonium salt	Aldehyde		
1	**17**	**24**		56 (*E*)
	19	**16**		52 (*E*)
2	**17**	**16**	92/8 (*Z*/*E*)	75 (*Z*)
3	**22**	**20**	93/7 (*Z*/*E*)	56 (*Z*)
4	**22**	**16**	91/9 (*Z*/*E*)	52 (*Z*)
	17	**20**		60 (*Z*)
5	**17**	**23**	65/35	35
6	**22**	**24**	65/35 (*Z*/*E*)	55

[a] Measured as the ratio of ^1H NMR signals ($N–CH_3$) for the spirooxazine unit, H-2 for the naphthopyran one. NMR spectra were monitored using products purified by liquid chromatography but not recrystallised.

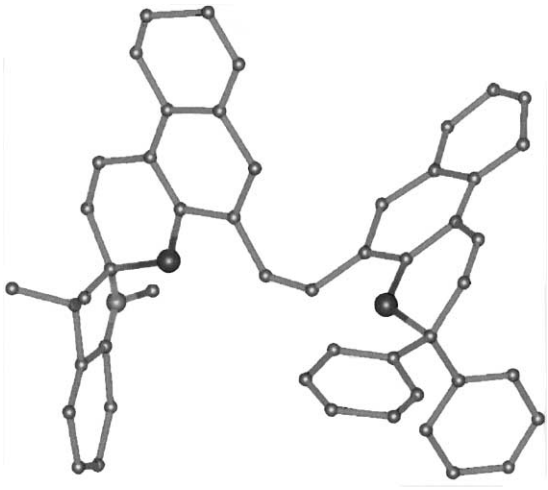


Figure 1. Balls and Sticks representation of the molecular structure of compound **4**.

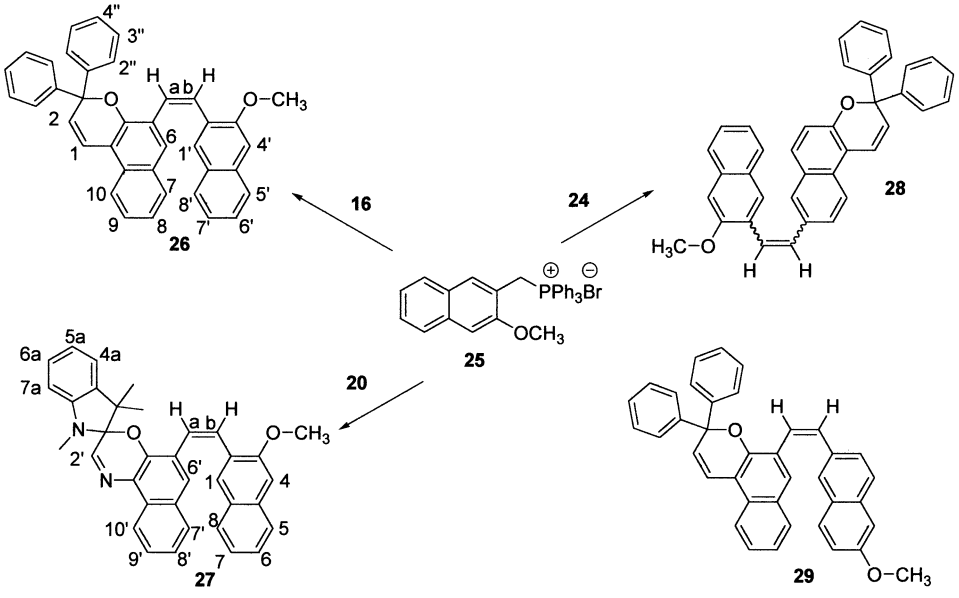
isomers were obtained. The configuration being certainly of importance regarding the photochromic behaviour, the major isomer has been isolated when possible (Table 1). Then compounds **1**–**4** were isolated as one pure isomer. In contrast, compounds **5** and **6** were obtained as unseparable mixtures.

In the case of the biphotochrome **4**, the *Z*-configuration of the isolated isomer has been proved by ^{1}H NMR spectrometry (6.75 and 6.92 ppm, respectively, for H_a and H_b, J_{ab}=12.4 Hz) and definitely confirmed by X-ray crystallography (Fig. 1). Unfortunately this structural assignment is not possible for the symmetrical compounds **2** (binaphthopyran) and **3** (bispirooxazine) for which the coupling between the H_a and H_b protons can not be observed under the NMR-technique applied. Finally, to establish the exact configuration of the major isomer, two model molecules **26**, **27** (to compare with **2** and **3**, respectively) in which a methoxy-substituted naphthalenic part mimics a photochromic unit, have been synthesised starting from the phosphonium salt **25** (Scheme 4). As for **2**, **3** and **4**, these compounds have been obtained as *Z*/*E* mixture with a highly predominant isomer (95:5, 93:7, respectively, for **26** and **27**), which was easily isolated.

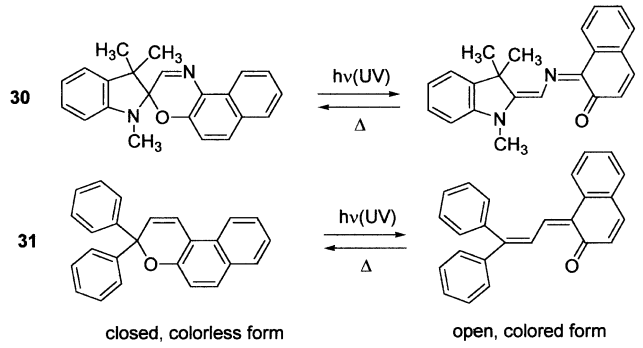
In both cases the *Z*-configuration of this isomer has been confirmed by ^{1}H NMR (coupling constant J_{ab}=12.4 Hz). Taking into account the structural similarity of biphotochromes **2** and **3** with the model compounds **26**, **27**, one can reasonably assume a *Z*-configuration for the double bond of the first ones. Moreover, if prepared monocrystals of **2** were not of sufficient quality to obtain a complete structure resolution by X-ray radiocrystallography, the *Z* stereochemistry of the central double bond has been confirmed for this compound.

To facilitate the identification of the stereochemistry of the isolated isomer for compound **1**, two model molecules **28** and **29** have been synthesised (Scheme 4), the latest been prepared from the phosphonium salt **17** and the 6-methoxy-2-naphthaldehyde. In both cases a mixtures of isomers has been obtained and a pure *E*-isomer has been isolated only with **29**. The comparison of ^{1}H NMR spectra of model molecules and compound **1** allows to assign to this one the *E*-configuration. This conclusion takes into account two main data: (i) the NMR spectrum of **1** does not show any signal between 6.70 and 7.20 ppm, while Ha and Hb protons of *Z*-**28** and *Z*-**29** appear in this range; (ii) signals of H-6 for compounds **1** and *E*-**29** are shifted to low field (7.94 and 7.95 ppm, respectively) compared to the shift of the same proton for biphotochromics and models of *Z*-configuration in which the double bond is linked to the 5-position (**2**, **4**, **26**, *Z*-**29**).

Then the structural elucidation of the new compounds has more especially shown that as well biphotochromics linked from 5 and for 5′ positions by a double bond (**2**–**4**) as their model compounds (**26** and **27**) exhibited curiously a major *Z*-configuration.



Scheme 4.



Scheme 5.

2.2. Photochromic behaviour

When submitted to UV irradiation, spirooxazines and diarylnaphthopyrans undergo generally a thermal reversible colour change due to the C–O bond cleavage (Scheme 5).[3]

The photochromic behaviour of biphotochromic compounds **1**–**6** and model compounds **26**–**28** has been evaluated under continuous irradiation (Xenon lamp) at room temperature using toluene as solvent. Details of conditions is given in the Section 3. Results are summarised in Table 2.

The characteristic parameters of unsubstituted 1,3,3-trimethylspiro[indoline–naphthoxazine] **30** and 3,3-diphenyl-naphthopyran **31** (Scheme 5) are given as references data.

Among the six new biphotochromic compounds (**1**–**6**) only **1**, **5** and **6** show expected thermally reversible photochromic properties which can be compared to those of **30** and **31**. Concerning binaphthopyrans **1** the comparison with the photochromic parameters of the model compounds **26** shows unambiguously (regarding especially the absorption wavelength of coloured form) that only one pyran unit is opened.

On the other hand the biphotochromic system **5** associating one spirooxazine unit and one chromene unit undergoes upon UV excitation the opening of both photochromic entities. The photochromic properties of **5** can be considered as the superposition of the properties of the spirooxazine and the chromene taken separately. Indeed, the coloured form of **5** shows two absorption bands in the visible range (447 and 612 nm) which can be attributed, respectively, to chromenic and spirooxazinic moieties (comparison with **30** and **31**). The behaviour of **6** is very similar of the **5** one. When the irradiation is stopped, each bond decreases according to the thermal kinetic of each species. The times for colouration (reaching of the photostationary state) and thermal fading in the case of **1**, **5** and **6** are in the range of few seconds, values which are generally observed in these families of photochromes.[32,33]

Table 2. Photochromic parameters obtained under continuous irradiation (150 W Xenon lamp, 10^{-4} M in toluene, 25°C)

Compounds	λ_{max} (nm)	A_∞	k_Δ (s^{-1})[a]
1	446	0.56	0.04
2	490[b]	0.40[c]	≅0
3	447	0.70[c]	≅0
	610	1.20[c]	
4	592	1.10[c]	≅0
5	447	0.20	0.05
	612	0.10	0.15
6	490	0.08	0.12
	592	0.18	0.18
26	430–450	0.50[c]	≅0
27	550[b]	0.50[c]	≅0
28	484	0.28	0.07
30	592	0.04	0.15
31	432	0.1	0.08

[a] Only the kinetic of higher amplitude (>80%) is given.
[b] Wide band.
[c] Compounds for which the photostationary state can not be reached. The absorbency is measured after 4 min of irradiation.

The other three compounds (**2**–**4**) have shown very slow colouration rates and thermal fading rates closed to zero. In these conditions, the times of irradiation necessary to reach a photostationary equilibrium are large (several dozen of minutes) and able to undergo degradation reactions. It is the reason why the samples were irradiated during four minutes only before monitoring the absorption spectrum in the visible range.

Compound **4** (in which the chromenic unit is linked to the 5′ position of the spirooxazine unit) leads to the formation of only one band near 590–600 nm. It seems that, in the experimental conditions used, only the oxazinic ring is opened, the naphthopyran acting simply as a conjugated substituent (comparison of **4** and **6** with the model compound **27**).

In the case of compound **2** in which two naphthopyrans are linked via the 5-position an alone wide absorption band (460–490 nm) is observed characteristic of the coloured form of this family of compounds. But one cannot precise if one or two pyran rings are opened, the molecule being completely symmetrical. The bathochromic shift (about 30 nm) observed, compared to the model molecule **26**, can be explained by the extension of conjugated system.

Concerning the compounds **3**, including two spirooxazine units linked through the 5′-position, the band corresponding to the coloured form of the oxazine is effectively observed (610 nm), but a second band of weaker intensity occurs also at 447 nm (Fig. 2). It should to be noted that this specific behaviour is observed in a lesser extent in the case of the model compound **27** which includes only one oxazine entity (Fig. 2, shoulder at 465 nm). A possible explanation could be related to the interaction between the two opened systems as proposed during the study of the thermochromism of bis-spiropyrans,[34] but the actual origin of this band is difficult to explain from the obtained spectroscopic results.

As mentioned above, whole compounds **2**–**4** and model compounds **26** and **27** lead under irradiation to thermally stable coloured forms (several days to several weeks in the dark). To our knowledge, it is the first time that bistable systems are described in spirooxazine and chromene series. Indeed, we have shown a possible photochemical decolouration using visible light in the case of compound **3** (Fig. 3).

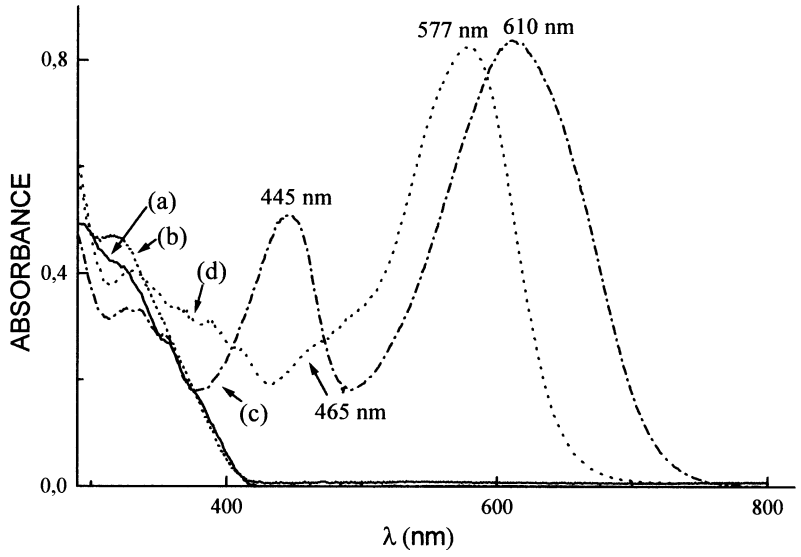


Figure 2. UV–Visible spectra of uncoloured [(ab)] and coloured forms [(cd)] of compounds **3** and **27**, respectively (toluene, 10^{-4} M, 20°C).

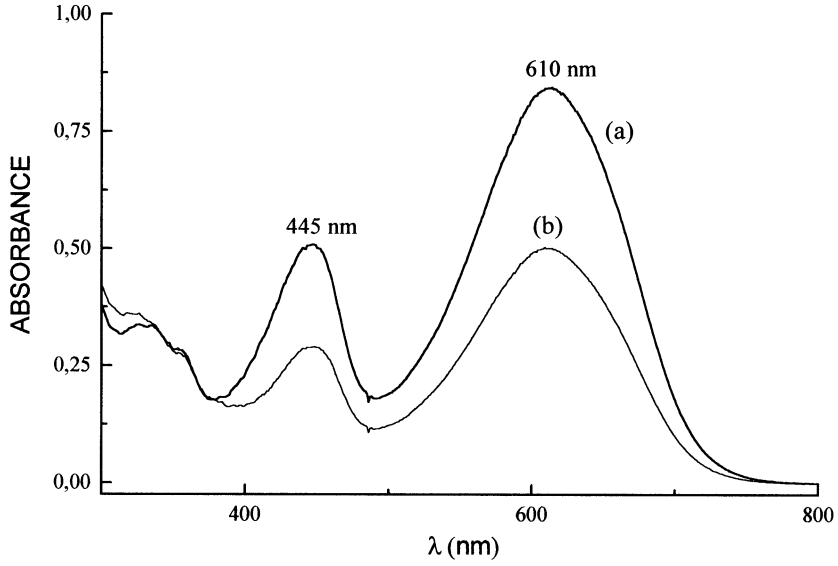
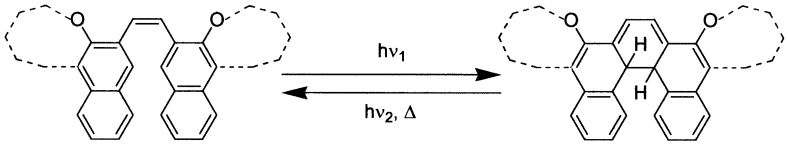


Figure 3. Example of the photobleaching of the coloured form of **3** under UV–Visible irradiation. Spectra of compound **3** (toluene 10^{-4} M, 20°C), after 4 min of UV irradiation by a Xenon lamp (spectrum (a)) followed by 10 min of visible irradiation (light of a Xenon lamp filtered by a GG 400 filter) (spectrum (b)).



Scheme 6.

Regarding the thermal stability of photoinduced forms, the behaviour of some of the new photochromic systems linked by an ethylenic junction is unusual compared to molecules taken individually. At this stage of our investigations we cannot explain this phenomenon (stabilisation due to the extension of the π system, possible photochemical *cis–trans* isomerisation of the central double bond). The fact that stable systems involved two photochromic units linked via the 5 or 5′ positions by a double bond of *Z*-configuration, makes also possible the occurrence of electrocyclisation reaction between the two aromatic systems as observed in photochromic *cis*-stilbenes (Scheme 6).[35] In this case, these new photochromics can act as photochemical multiswitches systems. Further experiments, and especially a NMR study

under UV irradiation, in progress, could lighten these points in a near future.

3. Experimental

3.1. Materials and methods

Solvents (SDS Company, France) were used without further purification other than drying over molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker BM 250 spectrometer (250 and 62.5 MHz, respectively, for ^{1}H and ^{13}C) using tetramethylsilane as internal standard. Chemical shifts are given in ppm and coupling constants in Hz. Melting points (°C),measured in capillary tubes on a Buchi 510 apparatus, are uncorrected. Column chromatography was performed on silica gel Merck 60 (70–230 mesh). Elemental analysis was performed by the Microanalytical Center of the University of Aix-Marseille III. The ion impact mass spectra were recorded on JEOL SX102 spectrometer. Photochromic measurements were performed in toluene solutions of spectrometric grade (Aldrich) at 20°C (to ±0.2°). The analysis cell (optical pathlength 10 mm) was placed in a thermostated copper block inside the sample chamber of a Beckman-DU-7500-diode-array spectrophotometer. An Oriel 150 W high pressure Xe lamp was used for irradiation. The identification of previously reported compounds were made by ^{1}H NMR and melting points comparison with literature data.

3.2. Starting materials

1,1-Diphenylpropyn-1-ol (Interchim), 6-methoxy-2-naphthaldehyde (Avocado), 2-methylene-1,3,3-trimethylindoline (Aldrich) and Dess–Martin periodinane (Lancaster) were commercially available. Compounds **7**,[27] **9**,[20] **10**,[36] **16**,[20] **20**,[26] **24**,[20] **25**,[37] were prepared according to previously described methods.

3.2.1. 6-Hydroxymethyl-2-naphthol (8). A solution of 2.2 g (12.8 mmol) of 6-hydroxy-2-naphthaldehyde in 50 ml of dry THF was added slowly to a stirred suspension of 0.5 g (13.1 mmol) of lithium aluminium hydride in 30 ml of the same solvent at 0°C (argon atmosphere). After 2 h stirring at ambient temperature, the mixture was carefully acidified with a solution (2N) of hydrochloric acid and extracted several times with Et_2O. The combined organic extracts were washed with water, dried with $MgSO_4$ and evaporated. Crystallisation gave 1.8 g (81%) of white solid, mp 169 (from ethanol) ^{1}H NMR (DMSO-d_6): 4.58(2H, d, J=4.9 Hz, CH_2); 5.27(1H, t, J=4.9 Hz, OH); 7.03–7.08(2H, m, H-1, H-3); 7.34(1H, dd, J=8.4 and 1.4 Hz, H-7); 7.62(1H, d, J=8.4 Hz, H-4); 7.66(1H, s, H-5); 7.71(1H, d, J=8.4 Hz, H-8); 9.73(1H, s, Ar–OH).

3.2.2. 3,3-Diphenyl-8-hydroxymethyl-[3*H*]-naphtho[2,1-*b*]pyran (11). A solution of 1.0 g (5.7 mmol) of 6-hydroxymethyl-2-naphthol **8**, 1.2 g (5.7 mmol) of 1,1-diphenyl-2-propyn-1-ol and a catalytic amount of *p*-toluensulfonic acid, in 100 ml of CH_3CN were stirred 12 h, at ambient temperature. After evaporation of the solvent, the residue was purified by column chromatography, eluent pentane/CH_2Cl_2 (30:70). Crystallisation gave 1.53 g (75%) of white solid, mp 86 (from heptane). ^{1}H NMR ($CDCl_3$): 1.66(1H, t, J=5.8 Hz, OH); 4.80(2H, d, J=5.8 Hz, CH_2); 6.28(1H, d, J=10.0 Hz, H-2); 7.10–7.27(8H, m, H-1, H-5, H-3′, H-4′); 7.35–7.42(5H, m, H-6, H-2′); 7.65(1H, d, J=8.7 Hz, H-9); 7.69(1H, s; H-7); 7.96(1H, d, J=8.7 Hz, H-10). ^{13}C NMR ($CDCl_3$): 65.3(t); 83.7(s); 115.2(s); 119.3(s); 120.0(d); 120.1(d); 123.0(d); 127.8(d); 128.5(d); 129.1(d); 129.3(d); 130.0(s); 130.1(d); 130.2(s) 130.8(d); 133.0(d); 144.8(s); 152.3(s). Anal. calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53; found: C, 85.63; H, 5.56.

3.2.3. 6-Hydroxymethyl-1-nitroso-2-naphthol (12). At 0°C, 3 ml of an aqueous sodium nitrite solution (20%) was added slowly to a solution of naphthol **8** (0.52 g, 3 mmol) in 5 ml of pyridine. Then, 10 ml of sulphuric acid (30%) was added over a period of 30 min. After stirring the mixture 1 h at 0°, the precipitate was collected by filtration, washed repeatedly with water and dried to give **12** as an orange powder which was used without further purification. Yield 0.55 g (90%), mp 139. ^{1}H NMR (Acetone-d_6): 4.51(1H, sl, OH); 4.75(2H, s, CH_2); 6.60(1H, m, H-3); 7.59(1H, d, J=7.7 Hz, H-7); 7.66(1H, s, H-5); 7.98(1H, m, H-4); 8.22(1H, m, H-8); 14.22(1H, sl, NOH).

3.3. General method for the synthesis of hydroxymethyl substituted spirooxazines

A solution of 0.173 g (1 mmol) of 2-methylene-1,3,3-trimethylindoline and 0.2 g (1.1 mmol) of corresponding 1-nitroso-2-naphthol (**10** or **12**) in 20 ml of trichloroethylene (ethanol for **10**) was refluxed for 5 h. After removing of the solvent under vacuum, compounds were purified by column chromatography on silica gel.

3.3.1. 5′-Hydroxymethyl-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphth[2,1-*b*][1,4]oxazine] (13). 55%, yield, eluent CH_2Cl_2. Crystallisation gave white cristals, mp 141 (from ethanol). ^{1}H NMR ($CDCl_3$): 1.35(3H, s, CH_3); 1.38(3H,s, CH_3); 1.91(1H, m, OH); 2.72(3H, s, N–CH_3); 4.62(1H, dd, J=13.6 and 7.0 Hz, H of CH_2); 4.73(1H, dd, J=13.6 and 5.9 Hz, H of CH_2); 6.55(1H, d, J=7.6 Hz, H-7); 6.89(1H, ddd, J=7.3, 7.3 and 0.8 Hz, H-5); 7.08(1H, dd, J=7.3 and 0.8 Hz); 7.21(1H, ddd, J=7.6,7.6 and 1.2 Hz, H-6); 7.42(1H, ddd, J=7.5, 7.5 and 1.1 Hz, H-8′); 7.57(1H, d, J=7.5, 7.5 and 1.1 Hz, H-9′); 7.71(1H, s, H-6′); 7.73(1H, d, J=8.4 Hz, H-7′); 7.79(1H, s, H-2′); 8.54(1H, d, J=8.4 Hz, H-10′); ^{13}C NMR ($CDCl_3$) 20.8(q); 25.4(q); 29.5(q); 51.5(s); 60.8(t); 98.5(s); 107.1(d); 120.0(d); 121.4(d); 121.5(d); 122.8(d); 124.5(d); 127.0(d); 127.8(d); 127.9(d); 128.1(d); 128.3(s); 128.8(s); 130.2(s); 135.7(s); 142.0(s); 147.1(s); 150.5(d). Anal. calcd for $C_{23}H_{22}N_2O_2$: C, 77.07; H, 6.19; N, 7.82; found: C, 77.11; H, 6.15; N, 7.80.

3.3.2. 8-Hydroxymethyl-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphth[2,1-*b*][1,4]oxazine] (14). 48% yield, eluent pentane/ether (40:60). Crystallisation gave white crystals, mp 178 (from ethanol). ^{1}H NMR ($CDCl_3$): 1.32(6H, s, CH_3); 2.28(1H, sl, OH); 2.72(3H, s, N–CH_3); 4.80(2H, sl, CH_2); 6.55(1H, d, J=7.6 Hz, H-7); 6.88(1H, dd, J=7.2 and 7.2 Hz, H-5); 6.99(1H, d, J=8.8 Hz, H-5′); 7.07(1H, d, J=7.2 Hz, H-4); 7.20(1H, ddd, J=7.6, 7.6 and 1.1 Hz, H-6); 7.54(1H, dd, J=8.7 and 1.5 Hz, H-9′);

7.60(1H, d, J=8.8 Hz, H-6′); 7.67(1H, s, H-7′); 7.71(1H, s, H-2′); 8.53(1H, d, J=8.7 Hz, H-10′). ^{13}C NMR ($CDCl_3$): 21.0(q); 25.7(q); 29.9(q); 52.1(s); 65.6(t); 98.8(s); 107.4(d); 117.3(d); 120.1(d); 121.7(d); 122.2(d); 123.2(s); 125.8(d); 126.8(d); 128.3(d); 129.4(s); 130.4(d); 130.5(s); 136.1(s); 137.0(s); 144.5(s); 147.8(s); 151.3(d). Anal. calcd for $C_{23}H_{22}N_2O_2$: C, 77.07; H, 6.19; N, 7.82; found: C, 77.12; H, 6.23; N, 7.72.

3.4. General method for the synthesis of bromomethyl substituted photochromes

A solution of 1.06 g (6.6 mmol) of bromine in 50 ml of anhydrous CH_2Cl_2 was added dropwise to a stirred solution of 2.15 g (8.5 mmol) of Ph_3P in 25 ml of the same solvent (argon atmosphere, ambient temperature). After 1 h stirring a resulting solution was added dropwise to a cooled (0°) solution of 5.5 mmol of hydroxymethyl substituted compound (**9** or **13**) in 50 ml of anhydrous CH_2Cl_2. After 2 h of additional stirring at ambient temperature the solution was washed with water, dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography on silica gel.

3.4.1. 5-Bromomethyl-3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]-pyran (15). 68% yield, eluent CH_2Cl_2. White solid, mp 126 (from heptane). ^{1}H NMR ($CDCl_3$): 4.65(2H, s, CH_2); 6.14(1H, d, J=10.0 Hz, H-2); 7.17–7.28(8H, m, H-1, H-8, H-3′, H-4′); 7.36–7.48(5H, m, H-9, H-2′); 7.62(1H, d, J=8.1 Hz, H-7); 7.64(1H, s, H-6); 7.88(1H, d, J=8.4 Hz, H-10). ^{13}C NMR ($CDCl_3$): 28.6(t); 83.1(s); 114.3(s); 119.5(d); 121.2(d); 124.0(d); 126.4(s); 127.0(d); 127.1(d); 127.5(d); 127.6(d); 128.5(d); 128.6(d); 128.7(s); 130.0(s); 130.6(d); 144.6(s); 148.2(s). Anal. calcd for $C_{26}H_{19}BrO$: C, 85.69; H, 5.53; found: C, 85.59; H, 5.45.

3.4.2. 5′-Bromomethyl-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphth[2,1-*b*][1,4]oxazine (21). 61% yield, eluent CH_2Cl_2. White solid, mp 156 (from heptane). ^{1}H NMR ($CDCl_3$): 1.34(3H, s, CH_3); 1.39(3H, s, CH_3); 4.44(1H, d, J=9.8 Hz, 1H of CH_2); 4.53(1H, d, J=9.8 Hz, 1H of CH_2); 6.56(1H, d, J=7.6 Hz, H-7); 6.90(1H, ddd, J=7.3, 7.3 and 0.8 Hz, H-5); 7.10(1H, dd, J=7.3 and 0.8 Hz, H-4); 7.21(1H, ddd, J=7.6, 7.6 and 1.2 Hz, H-6); 7.40(1H, dd, J=6.8 and 1.2 Hz, H-8); 7.58(1H, dd, J=6.8 and 1.2 Hz, H-9); 7.73(1H, d, J=8.4 Hz, H-7′); 7.75(1H, s, H-6′); 7.79(1H, s, H-2′); 8.54(1H, d, J=8.4 Hz, H-10′). ^{13}C NMR ($CDCl_3$): 20.9(q); 25.7(q); 27.6(t); 29.5(q); 51.6(s); 98.6(s); 107.2(d); 119.9(d); 121.4(d); 121.6(d); 123.2(s); 124.6(d); 125.4(s); 127.6(d); 127.8(d); 128.0(d); 128.5(s); 130.7(d); 131.0(s); 135.8(s); 141.9(s); 147.2(s); 150.5(d); Anal. calcd for $C_{23}H_{21}BrN_2O$: C, 65.57; H, 5.02; N, 6.65; found: C, 65.52; H, 5.06; N, 6.61.

3.4.3. 8-Chloromethyl-3,3-diphenyl-[3*H*]naphtho[2,1-*b*]-pyran (18). A solution of 0.42 g (3.5 mmol) of thionyl chloride in 5 ml of anhydrous Et_2O was added dropwise to cooled (0°) solution of 0.72 g (2 mmol) of compound **11** in 30 ml of anhydrous Et_2O. After 2 h stirring at ambient temperature the mixture was evaporated. The crude product was purified by column chromatography on silica gel, eluent pentane/CH_2Cl_2 (80:20) to give 0.38 g (50%) of white crystals. Mp 127 (from heptane). ^{1}H NMR ($CDCl_3$): 4.67(2H, s, CH_2); 6.26(1H, d, J=9.9 Hz, H-2); 7.18–7.33(8H, m, H-1, H-5, H-3′, H-4′); 7.46–7.48(5H, m, H-6, H-2′); 7.60(1H, d, J=8.7 Hz, H-9); 7.65(1H, s, H-7); 7.92(1H, d, J=8.7 Hz, H-10). ^{13}C NMR ($CDCl_3$): 46.5(t); 82.6(s); 114.0(s); 118.8(d); 119.3(d); 122.1(d); 126.9(d); 127.0(d); 127.5(d); 127.9(d); 128.0(d); 128.2(s); 128.9(s); 129.5(s); 129.8(d); 132.5(d); 144.6(s); 151.0(s). Anal. calcd for $C_{26}H_{19}ClO$: C, 81.56; H, 5.00; found: C, 81.48; H, 4.94.

3.5. General method for the synthesis of phosphonium salts

A mixture of 3 mmol of halogenomethyl substituted compound (**15**, **18** or **21**) and 3 mmol of triphenylphosphine was refluxed 12 h in 10 ml of anhydrous toluene (*o*-xylene for **18**). After cooling, the precipitate was filtered off, washed with cold toluene and dried.

3.5.1. (3,3-Diphenyl-[3*H*]naphtho[2,1-*b*]pyran-5-yl)methyltriphenylphosphonium bromide (17). 90% yield. White solid, mp 257. ^{1}H NMR ($CDCl_3$): 5.41(2H, d, J=14.1 Hz, CH_2); 6.16(1H, d, J=10.0 Hz, H-2); 7.03–7.75(30H, m, H-arom. and H-1); 7.87(1H, d, J=8.5 Hz, H-10).

3.5.2. (3,3-Diphenyl-[3*H*]naphtho[2,1-*b*]pyran-8-yl)methyltriphenylphosphonium chloride (19). 59% yield. White solid, mp 253. ^{1}H NMR ($CDCl_3$): 5.44(2H, d, J=14.3 Hz, CH_2); 6.22(1H, d, J=9.9 Hz, H-2); 7.05–7.68(31H, m, H-arom. and H-1).

3.5.3. (1,3,3-Trimethylspiro[indoline-2,3′-[3*H*]naphtho-[2,1-*b*][1,4]oxazine]-5-yl) methyltriphenylphosphonium bromide (22). 92% yield. White solid, mp 238. ^{1}H NMR ($CDCl_3$): 0.95(3H, s, CH_3); 1.25(3H, s, CH_3); 2.12(3H, s, N–CH_3); 4.95(1H, dd, J=14.7 and 14.7 Hz, 1H of CH_2); 5.61(1H, dd, J=14.7 and 14.7 Hz, 1H of CH_2); 6.49(1H, d, J=7.7 Hz, H-7); 7.02(1H, dd, J=7.1 and 7.1 Hz, H-5); 7.1(1H, d, J=7.1 Hz, H-4); 7.31–7.76(20H, m, H-arom. and H-2′); 7.93(1H, d, J=3.5 Hz, H-6′); 8.49(1H, d, J=8.4 Hz, H-10′).

3.5.4. 8′-Formyl-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]-naphth[2,1-*b*][1,4]oxazine] (23). A solution of 0.36 g (1 mmol) of spirooxazine **14** in 20 ml of dry CH_2Cl_2 was added slowly to a solution of 0.42 g (1 mmol) of Dess–Martin periodinane in 40 ml of the same solvent. After 1 h stirring, 50 ml of ether was added and mixture filtered on celite. After evaporation of the solvent, the residue was purified by column chromatography (eluent CH_2Cl_2) to give 0.21 g (59%) of yellow crystals. Mp 201 (from heptane). ^{1}H NMR ($CDCl_3$): 1.35(3H, s, CH_3); 1.37(3H, s, CH_3); 2.79(3H, s, N–CH_3); 6.59(1H, d, J=7.7 Hz, H-7); 6.91(1H, dd, J=7.4 and 7.4 Hz, H-5); 7.08–7.12(2H, m, H-4 and H-5′); 7.21(1H, ddd, J=7.2, 7.2 and 1.5 Hz, H-6); 7.79(1H, s, H-2′); 7.82(1H, d, J=8.9 Hz, H-6′); 8.04(1H, dd, J=8.7 and 1.5 Hz, H-9′); 8.24(1H, s, H-7′); 8.66(1H, d, J=8.7 Hz, H-10′); 10.12(1H, s, CHO). ^{13}C NMR ($CDCl_3$): 20.9(q); 25.7(q); 29.8(q); 52.3(s); 99.4(s); 107.5(d); 118.4(d); 120.3(d); 121.7(d); 122.9(d); 123.4(s); 124.6(d); 128.3(d); 128.5(s); 132.1(d); 132.9(s); 134.3(d); 134.4(s); 135.8(s); 147.1(s); 147.6(s); 151.8(d); 192.2(d). Anal. calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86; found: C, 77.65; H, 5.56; N, 7.64.

3.6. General method for the synthesis of biphotochromic compounds and models

A 50% solution of NaOH (3 ml) was added to a stirred solution of 1 mmol of phosphonium salt and 1 mmol of aldehyde in 3 ml of CH_2Cl_2. After 2 h stirring 30 ml of CH_2Cl_2 and 30 ml of water were added. The organic phase was washed with water, dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography on silica gel.

3.6.1. 5-[2-(3,3-Diphenyl-[3*H*]naphtho[2,1-*b*]pyran-8-yl)-ethenyl]-3,3-diphenyl-[3*H*]naphtho[2,1-*b*]pyran (1). Eluent pentane/CH_2Cl_2 (70:30). Pale yellow solid, mp 238 (from heptane). ^1H ($CDCl_3$) NMR: 6.27(1H, d, J=9.9 Hz, H-2′); 6.29(1H, d, J=9.9 Hz, H-2); 7.18–7.78(31H, m, H-arom., Ha, Hb, H-1,H-1′; 7.88–7.95(2H, m, H-10 and H-10′); 7.94(1H, s, H-6). Anal. calcd for $C_{52}H_{36}O_2$: C, 90.15; H, 5.24; found: C, 90.07; H, 5.28. m/z 692 (M^+).

3.6.2. 1,2-Bis(3,3-diphenyl-[3*H*]naphtho[2,1-*b*]pyran-5-yl)ethylene (2). Eluent pentane/ether (90:10). Yellow solid, mp 228 (from heptane). ^1H NMR ($CDCl_3$): 6.30(2H, d, J=9.9 Hz, H-2); 7.00–7.34(24H, m, H-arom., H-a and H-1); 7.55(8H, d, J=7.2 Hz, H-2′); 7.86(2H, d, J=8.5 Hz, H-10). ^{13}C NMR ($CDCl_3$): 82.7(s); 114.7(s); 120.3(d); 121.1(d); 123.5(d); 126.4(d); 126.8(d); 126.9(d); 127.0(d); 127.6(d); 128.3(d); 128.8(d); 128.9(d); 129.2(s); 129.7(d); 145.0(s); 149.2(s). Anal. calcd for $C_{52}H_{36}O_2$: C, 90.15; H, 5.24; found: C, 90.11; H, 5.19. m/z 692 (M^+).

3.6.3. 1,2-Bis(1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphth-[2,1-*b*][1,4]oxazin-5′-yl)ethylene (3). Eluent pentane/CH_2Cl_2 (20:80). Grey solid, mp 249 (from heptane). ^1H NMR ($CDCl_3$): 1.31(6H, s, CH_3); 1.34(6H, s, CH_3); 2.66(3H, s, N–CH_3); 2.69(3H, s, N–CH_3); 6.49(2H, d, J=7.7 Hz, H-7); 6.56(2H, s, H-a); 6.85(2H, dd, J=7.4 and 7.4 Hz, H-5); 7.03(2H, d, J=7.1 Hz, H-4); 7.17(2H, dd, J=7.6 and 7.6 Hz, H-6); 7.23(2H, dd, J=8.1 and 8.1 Hz, H-8′); 7.33(2H, d, J=8.0 Hz, H-7′); 7.49(2H, dd, J=7.1 and 7.1 Hz, H-9′); 7.62(2H, s, H-6′); 7.73(2H, s, H-2′); 8.48(2H, d, J=8.3 Hz, H-10′). ^{13}C NMR ($CDCl_3$): 21.5(q); 25.6(q); 29.7(q); 51.9(s); 98.9(s); 107.1(d); 119.8(d); 121.5(d); 121.6(d); 124.4(d); 125.1(d); 127.1(d); 128.0(d); 128.1(d); 128.6(s); 129.2(d); 130.4(s); 135.9(s); 147.6(s); 151.3(d). Anal. calcd for $C_{46}H_{40}N_4O_2$: C, 81.15; H, 5.92; N, 8.23; found: C, 81.12; H, 5.91; N, 8.19. m/z 681 (MH^+).

3.6.4. 5′-[2-(3,3-Diphenyl-[3*H*]naphtho[2,1-*b*]pyran-5-yl)-ethenyl]-1,3,3-trimethylspiro [indoline-2,3′-[3*H*]naphth-[2,1-*b*][1,4]oxazine] (4). Eluent pentane/ether (95:5). White solid, mp 212 (from heptane). ^1H NMR ($CDCl_3$): 1.37(6H, s, CH_3); 2.71(3H, s, N–CH_3); 6.26(1H, d, J=9.8 Hz, H-2); 6.56(1H, d, J=7.7 Hz, H-7a); 6.75(1H, d, J=12.4 Hz, H-a); 6.89(1H, dd, J=7.3 and 7.3 Hz, H-5a); 6.92(1H, d, J=12.4 Hz, H-b); 7.09(1H, d, J=7.3 Hz, H-4a); 7.15–7.49(20H, m, H-arom.); 7.75(1H, s, H-2′); 7.91(1H, d, J=8.4 Hz, H-10); 8.48(1H, d, J=8.4 Hz, H-10); 8.48(1H, d, J=8.4 Hz, H-10′). ^{13}C NMR ($CDCl_3$); 21.3(q); 25.5(q); 29.6(q); 51.9(q); 82.7(s); 98.9(s); 107.1(d); 114.9(s); 119.8(d); 120.1(d); 121.2(d); 121.3(d); 121.6(d); 123.0(s); 123.7(d); 124.1(d); 124.9(d); 125.3(s); 126.5(d); 126.9(d); 127.5(d); 127.6(d); 128.1(d); 128.2(d); 128.4(d); 128.5(s); 128.6(d); 128.9(s); 129.2(d); 129.3(s); 129.7(d); 130.3(s); 136.0(s); 142.5(s); 144.8(s); 144.9(s); 147.7(s); 148.9(s); 151.0(d). Anal. calcd for $C_{49}H_{38}N_2O_2$: C, 85.69; H, 5.58; N, 4.08; found: C, 85.60; H, 5.59; N, 4.06. m/z 687 (MH^+).

Crystal data for **4** ($C_{49}H_{38}N_2O_2$) M_r=686.85, monoclinic, a=10.949(2), b=28.165(6), c=11.762(2) Å, β=94.69(2)°, V=3615(12) Å^3, space group $P2_1/c$, Z=4, D_c=1.261 Mg m^{-3}, $F(000)$=1408, μ=0.074 mm^{-1}, T=293 K, θ=0–35°, $0<h<11$, $0<k<28$, $-12<l<12$, reflections collected 4934, independent reflections 4934 (full-matrix least-squares on F^2). Crystal being of poor quality hydrogen atoms were not located. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center.

3.6.5. 8′-[2-(3,3-Diphenyl-[3*H*]naphtho[2,1-*b*]pyran-5-yl)-ethenyl]-1,3,3-trimethylspiro [indoline-2,3′-[3*H*]naphth-[2,1-*b*][1,4]oxazine] (5). Eluent CH_2Cl_2. Yellow solid, mp 158 (from heptane). ^1H NMR ($CDCl_3$): Major isomer: 1.34(6H, s, CH_3); 2.75(3H, s, N–CH_3); 6.29(1H, d, J=9.9 Hz, H-2); 6.55(1H, d, J=7.6 Hz, H-7a); 6.85–7.95(26H, m, H-arom., H-1, H-2′, H-a, H-b); 8.57(1H, d, J=8.8 Hz, H-10′).

Minor isomer 1.32(6H, s, CH_3); 2.71(3H, s, N–CH_3); 6.30(1H, d, J=9.9 Hz, H-2); 6.53(1H, d, J=7.6 Hz, H-7a); 6.85–7.95(26H, m, H-arom., H-1, H-2′, H-a, H-b); 8.23(1H, d, J=8.8 Hz, H-10′). Anal. calcd for $C_{49}H_{38}N_2O_2$: C, 85.69; H, 5.58; N, 4.08; found: C, 85.58; H, 5.49; N, 4.05. m/z 687 (MH^+).

3.6.6. 5′-[2-(3,3-Diphenyl-[3*H*]naphtho[2,1-*b*]pyran-8-yl)-ethenyl]-1,3,3-trimethylspiro [indoline-2,3′-[3*H*]naphth-[2,1-*b*][1,4]oxazine] (6). Eluent pentane/ether (95:5), white solid mp 230 (from heptane). ^1H NMR ($CDCl_3$): Major isomer (*Z*): 1.37(3H, s, CH_3); 1.41(3H, s, CH_3); 2.75(3H, s, N–CH_3); 6.25(1H, d, J=9.5 Hz, H-2); 6.52(1H, d, J=12.6 Hz, H-a); 6.62(1H, d, J=7.5 Hz, H-7a); 6.65(1H, d, J=12.6 Hz, H-b); 6.97–7.85(24H, m, H-arom., H-2′, H-1); 8.50(1H, d, J=8.3 Hz, H-10′).

Minor isomer (*E*) 1.33(6H, s, CH_3); 2.66(3H, s, N–CH_3); 6.21(1H, d, J=9.5 Hz, H-2); 6.48(1H, d, J=7.5 Hz, H-7a); 6.88(1H, dd, J=7.8 and 7.8 Hz, H-5a); 6.97–7.85(24H, m, H-arom., H-2′, H-1); 8.50(1H, d, J=8.3 Hz, H-10′). Anal. calcd for $C_{49}H_{38}N_2O_2$: C, 85.69; H, 5.58; N, 4.08; found: C, 85.60; H, 5.59; N, 3.95. m/z 687 (MH^+).

3.6.7. 3,3-Diphenyl-5-[2-(3-methoxy-2-naphthyl)ethenyl]-[3*H*]naphtho[2,1-*b*]pyran (26). Eluent CH_2Cl_2. Pale yellow solid, mp 144 (from heptane). ^1H NMR ($CDCl_3$): 3.89(3H, s, OCH_3); 6.32(1H, d, J=9.9 Hz, H-2); 6.97(1H, d, J=12.3 Hz, H-a); 7.07–7.15(4H, m, H-b, H-4′, H-6′ and H-7′); 7.20–7.37(12H, m, H-arom., H-1); 7.47(1H, s, H-1′); 7.55(4H, m, H-2″); 7.66(1H, d, J=8.2 Hz, H-7); 7.89(1H, d, J=8.5 Hz, H-10). ^{13}C NMR ($CDCl_3$): 55.7(q); 82.8(s); 105.4(d); 114.9(s); 120.4(d); 121.3(d); 123.6(d); 123.7(d); 126.3(d); 126.4(d); 126.5(d); 126.6(d); 127.0(d); 127.2(d); 127.3(s); 127.7(d); 128.1(d); 128.4(d); 128.7(s); 128.8(d); 129.0(s); 129.4(d); 129.5(d); 134.1(s); 145.1(s); 149.2(s);

156.3(s). Anal. calcd for $C_{38}H_{28}O_2$: C, 88.34; H, 5.16; found: C, 88.39; H, 5.13.

3.6.8. 5′-[2-(3-Methoxy-2-naphthyl)ethenyl]-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphth[2,1-*b*][1,4]oxazine] (27). Eluent CH_2Cl_2, White solid, mp 204 (from heptane). ^{1}H NMR ($CDCl_3$): 1.37(3H, s, CH_3); 1.40(3H, s, CH_3); 2.72(3H, s, N–CH_3); 3.85(3H, s, OCH_3); 6.55(1H, d, *J*=7.7 Hz, H-7a); 6.71(1H, d, *J*=12.4 Hz, H-a); 6.79(1H, d, *J*=12.4 Hz, H-b); 6.88(1H, dd, *J*=7.4 and 7.4 Hz, H-5a); 7.08(1H, d, *J*=7.4 Hz, H-4a); 7.10(1H, s, H-4); 7.15–7.24(3H, m, H-6, H-6a, H-7); 7.28–7.49(m, 4H, H-8, H-5, H-8′, H-9′); 7.58(1H, s, H-1); 7.61(1H, s, H-6′); 7.68(1H, d, *J*=8.1 Hz, H-7′); 7.75(1H, s, H-2′); 8.47(1H, d, *J*=8.4 Hz, H-10′). ^{13}C NMR ($CDCl_3$):21.3(q); 25.5(q); 29.5(q); 51.8(s); 55.5(q); 98.7(s); 105.3(d); 106.9(d); 119.6(d); 121.2(d); 121.5(d); 123.0(s); 123.6(d); 124.1(d); 124.4(d); 125.5(s); 126.2(d); 126.3(d); 126.8(d); 127.3(d); 127.7(d); 127.9(d); 128.5(s); 128.7(d); 129.3(d); 130.1(s); 134.0(s); 142.3(s); 147.6(s); 151.1(d); 155.9(s). Anal. calcd for $C_{35}H_{30}N_2O_2$: C, 82.32; H, 5.92; N, 5.48; found: C, 82.28; H, 6.02; N, 5.36.

3.6.9. 3,3-Diphenyl-8-[2-(3-methoxy-2-naphthyl)ethenyl]-[3*H*]naphtho[2,1-*b*]pyran (28). Eluent pentane/ether (85:15). White solid, mp 208 (from heptane). ^{1}H NMR ($CDCl_3$): Major isomer (*E*): 3.96(3H, s, OCH_3); 6.25(1H, d, *J*=9.9 Hz, H-2); 7.10–7.78(22H, m, H-arom., H-a, H-b, H-1); 7.89(1H, d, *J*=9.0 Hz, H-10); 8.02(1H, s, H-7).

Minor isomer (*Z*) 3.89(3H, s, OCH_3); 6.17(1H, d, *J*=9.9 Hz, H-2); 6.79(2H, s, H-a and H-b); 7.10–7.78(22H, m, H-arom., H-1). Anal. calcd for $C_{38}H_{28}O_2$: C, 88.34; H, 5.16; found: C, 88.28; H, 5.10.

3.6.10. 3,3-Diphenyl-5-[2-(6-methoxy-2-naphthyl)ethenyl]-[3*H*]naphtho[2,1-*b*]pyran (29). Eluent pentane/ether (90:10). Pale yellow solid, mp 139 (from heptane). ^{1}H NMR ($CDCl_3$) (*E*-isomer): 3.92(3H, s, OCH_3); 6.30(1H, d, *J*=9.9 Hz, H-2); 7.12–7.15(2H, m, H-1′ and H-3′); 7.18–7.85(20H, m, H-arom., H-a, H-b,H-1); 7.90(1H, d, *J*=8.5 Hz, H-10); 7.95(1H, s, H-6). ^{13}C NMR ($CDCl_3$):55.3(q); 82.9(s); 105.9(d); 114.3(s); 119.0(d); 119.9(d); 121.2(d); 122.4(d); 123.9(d); 124.1(d); 126.0(d); 126.3(d); 126.7(d); 126.8(d); 127.1(s); 129.1(s); 129.3(s); 129.5(d); 130.9(d); 133.2(s); 134.2(s); 144.9(s); 148.5(s); 157.8(s). Anal. calcd for $C_{38}H_{28}O_2$: C, 88.34; H, 5.16; found: C, 88.38; H, 5.21.

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