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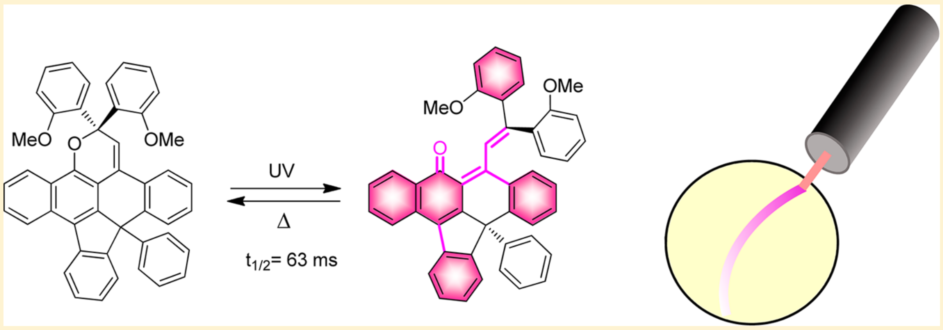
Fast Color Change with Photochromic Fused Naphthopyrans

Céu M. Sousa,[†] Jerome Berthet,[‡] Stephanie Delbaere,[‡] André Polónia,[†] and Paulo J. Coelho*,[†]

[†]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal

[‡]UDSL, CNRS UMR 8516, Faculté des Sciences Pharmaceutiques et Biologiques, Université Lille Nord de France, F-59006 Lille, France

Supporting Information



ABSTRACT: Photochromic molecules can reversibly develop color upon irradiation with UV light. These smart molecules, mainly in the naphthopyran family, have been applied with success to ophthalmic lenses that darken quickly under sunlight and revert to the uncolored state after several minutes in the dark. This slow adaptation to the absence of light is one of the limitations and is due to the formation of an unwanted photoisomer. We have designed a new naphthopyran with a bridged structure which prohibits the formation of the undesirable, persistent photoisomer and thus shows a very fast switching between the uncolored and colored states. UV irradiation of a hybrid siloxane matrix doped with the new fused naphthopyran leads to the formation of a pink coloration bleaching in a few milliseconds, in the absence of light, at room temperature. This new fused naphthopyran is easily prepared in three steps from readily accessible precursors and is amenable to structural modifications to tailor color and lifetime of the colored photoisomer.

INTRODUCTION

Photochromism is a reversible transformation, promoted by light, between two chemical species having different absorption spectra.[1] The photochemical process is associated with a unimolecular reaction, and if the photogenerated species absorbs in the visible region of the spectrum, a color change can be observed. The key feature of this phenomenon is reversibility. For classes of compounds such as diarylethenes,[2] the reversibility is photochemical with a specific wavelength of light (P-type), while for others like azobenzenes,[3] hexaarylbiimidazoles,[4] or naphthopyrans,[5] the photoinduced colored species is thermally unstable and reverts spontaneously to the initial form in the absence of light (T-type). This thermal switching has attracted the attention of industry for several decades, and the color change observed with some thermally reversible photochromic compounds was successfully explored to create ophthalmic lenses,[6] smart windows,[7] and textiles[8] that change their color reversibly upon exposure to sunlight. Among T-type compounds, naphthopyrans are the most used photochromic system, especially by the lens industry,[9] because they can be easily synthesized at a relatively low cost, are very sensitive to sunlight, can generate different colors, and show high resistance to fatigue.[10] UV irradiation of these compounds promotes the cleavage of the C(sp^3)−O bond of the pyran ring to afford two isomeric forms denoted as *transoid-cis* (TC) and *transoid-trans* (TT) (Figure 1), which are colored due to the extended conjugation connecting the naphthalene and the phenyl ring and absorb at similar λ_{max}. However, they are thermally unstable, being reverted with different speeds to the initial uncolored state.[11] While the TC photoisomer fades quickly (few seconds to minutes) to the closed form (NP), the TT is less labile and is slowly converted (minutes to hours) into the TC isomer, which then reverts to the uncolored state. The TT photoisomer is therefore responsible for the slow thermal response of this system and then for the persistent residual color.

These versatile compounds can be incorporated in polymeric matrices or organic−inorganic hybrids and applied as coatings on surfaces, although the color exhibited after light excitation and the decay kinetic can be strongly affected by the local environment.[12] The residual color commonly observed with these compounds, associated with the formation of the TT isomer, is an important problem for the lens industry. In fact, photochromic lenses are quickly activated by sunlight (<30 s) but exhibit a slow fading color in the dark (usually more than 5

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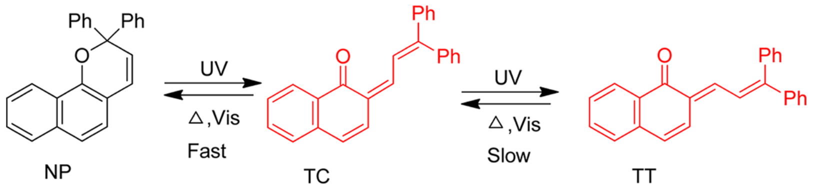

Figure 1. Photochromic equilibrium for the 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran.

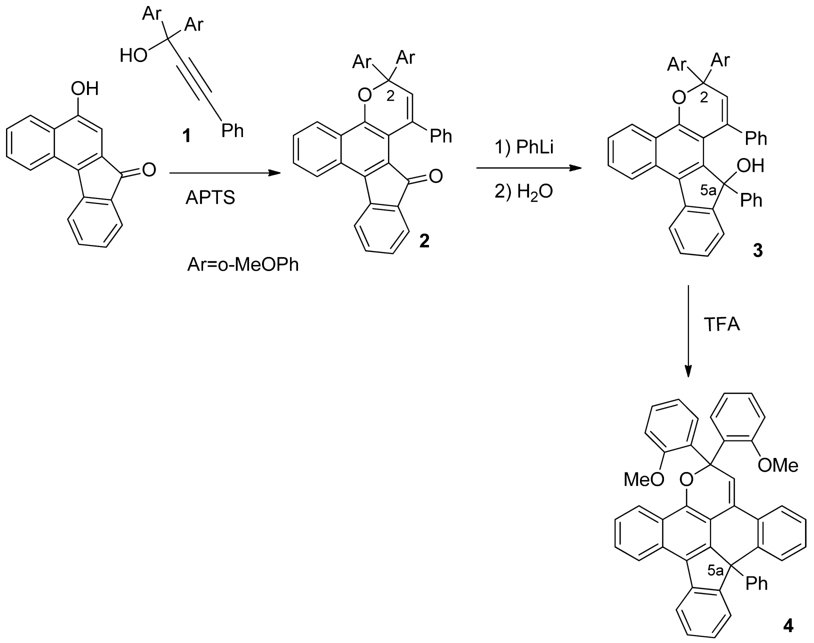

Figure 2. Synthesis of the fused naphthopyran **4**.

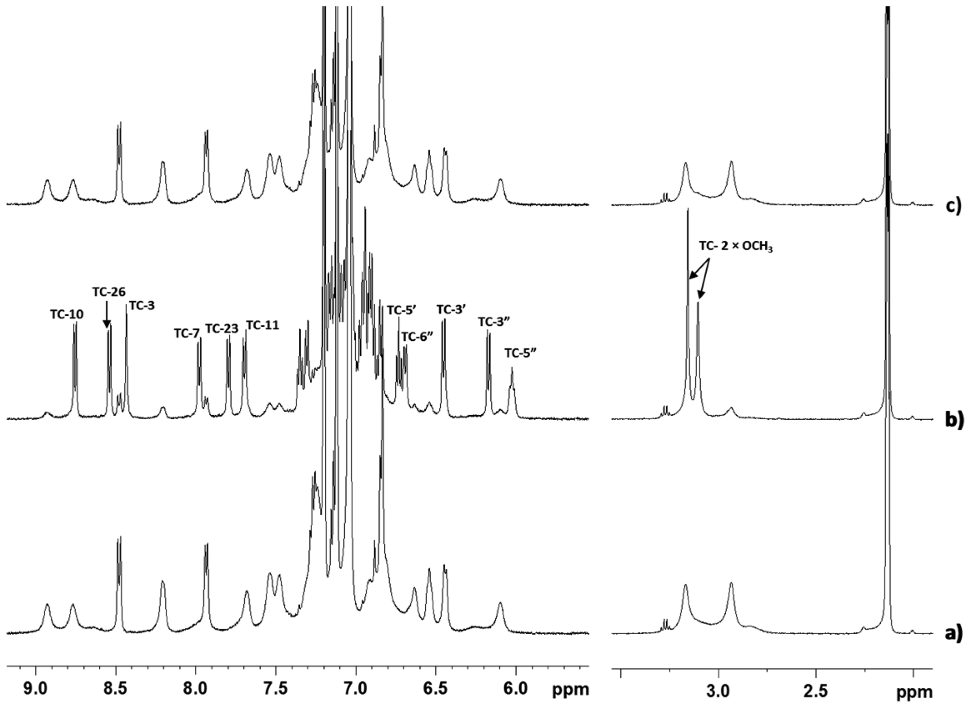

Figure 3. ^{1}H NMR spectra of compound **4** in toluene at −70 °C (a) before UV, (b) after UV (355 nm, 35 min), and (c) after thermal relaxation.

min), and once the wearer goes indoors, the lenses stay colored for too long. A fast switching system able to achieve intense colorations is thus actively sought by the lens industry. With this objective in mind, we have been looking for the structural modification of the naphthopyran core to design compounds where the formation of the persistent TT isomer would be impossible and the thermal relaxation of the TC isomer would be accelerated.[13] In addition, these two requirements must be coupled with an easy and rapid synthetic strategy, and the photochromic properties must be effective not only in solution but also in the polymer matrix. In the present work, we report a new naphthopyran derivative that answers to all these criteria. It contains a bridged structure substituent linking a 4-phenyl to an indene group, and to counterbalance the steric hindrance of the fused system, two *ortho*-methoxy groups in the C(sp^3)−2 phenyl rings were inserted to get a fast switching system[14] able to develop an intense color.

■ RESULTS AND DISCUSSION

We designed an easy route to this complex molecule starting from an indeno-annelated naphthol. The phenyl-substituted pyran ring was created by reaction with a phenyl-substituted propynol, and then the phenyl group was connected to the indene ring to afford the bridged system (Figure 2). Thus, the reaction of 2,2′-dimethoxybenzophenone with phenylacetylene in the presence of *n*-BuLi gave 1,1-bis(2-methoxyphenyl)-3-phenylprop-2-yn-1-ol **1** in good yield (64%).[15] This propargylic alcohol was then condensed with 5-hydroxy-7*H*-benzo[*c*]-fluoren-7-one, a red colored naphthol, in the presence of APTS, to afford the red naphthopyran **2**, which was treated with PhLi/THF at 0 °C to give the alcohol **3**. The mass increase from 572.18 to 650.61 *m*/*z* and the presence of one band at 3543 cm^{-1} in the IR spectrum confirmed the formation of alcohol **3**. In the ^1H NMR spectrum, a singlet signal at 2.09 ppm is observed, characterizing the alcohol function of the new cyclopentadiene cycle. Due to the steric hindrance and the asymmetric carbon C-5a at 80.7 ppm, the two *ortho*-methoxyphenyl groups at the sp^3 pyran carbon (C-2) become inequivalent and resonate as two singlets at 3.49 and 3.59 ppm. The intramolecular cyclization of naphthopyran **3** was tested with different acids such as *p*-toluenesulfonic acid, CH_3COOH, HCl, and H_2SO_4 without success. Nevertheless, the addition of trifluoroacetic acid, without any solvent, gave the expected fused naphthopyran **4** in 49% yield. The formation of the fused naphthopyran **4** was confirmed by the disappearance of the singlet signal of the alcohol function at 2.09 ppm. In addition, the sp^3 carbon C-5a was shielded from 80.7 to 57.7 ppm.

In situ laser (355 nm) irradiation coupled to a NMR spectrometer,[16] at room temperature, did not induce any color development of a toluene solution of **4**, while at −70 °C, a strong purple coloration was observed. NMR underlined the formation of a set of new signals that are characteristic of a single colored opened naphthopyran with a TC configuration, namely, a deshielded singlet signal at 8.48 ppm assigned to proton H-3 (Figure 3). Typical signals of the TT isomer were not observed. The structure of the open form was confirmed by 1D selective experiments and 2D experiments recorded at −70 °C. In 1D selective experiments, important dipolar correlations were observed: H-3′ (6.42 ppm)−methoxy (3.13 ppm); H-3″ (6.14 ppm)−methoxy (3.10 ppm); H-23 (7.78 ppm)−H-14 (7.27 ppm); H-7 (7.97 ppm)−H-11 (7.67 ppm) (Figure 4 and Supporting Information). The opened TC isomer was also characterized by a $^1H-^{13}C$ HMBC experiment that displayed long-range correlations between the characteristic carbonyl carbon C-1 at 184.6 ppm and the aromatic protons H-10 at 8.77 ppm. The thermal relaxation of the solution measured when light is off, at five temperatures between 193 and 213 K, gave access to the time evolution of concentrations. The only photoproduct, TC, follows a monoexponential decay with rates varying from 0.82×10^{-4} to 27.4×10^{-4} s^{-1}, associated with an activation energy of 59 kJ mol^{-1}. Therefore, unlike common naphthopyrans, the UV irradiation of the fused naphthopyran **4** produces only a fast decay colored photoisomer with a TC configuration (Figure 4).

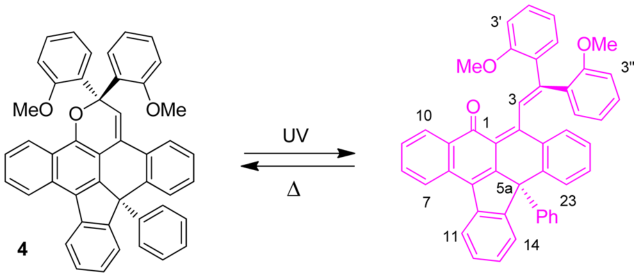

Figure 4. Photochromic equilibrium for the fused naphthopyran **4**.

Toluene solutions of the fused naphthopyran **4** are colorless with a strong absorption in the UV region. However, exposure of this solution to sunlight did not produce any visible color change because the sunlight power is too low to generate a high concentration of the short-lived colored species. Using a high-power laser (405 nm, 200 mW), it was possible to promote the photochemical isomerization at room temperature and to attain a photostationary equilibrium characterized by a high color intensity. The opened naphthopyran **4** has a broad absorption in the visible region with a maximum at 525 nm and a half-life time of 63 ms at 20 °C. This very fast switching system allows the coloration of the solution only where the laser light is focused. Once the light moves, the colored zone follows the light (Figure 5 and video 1 in the Supporting Information).

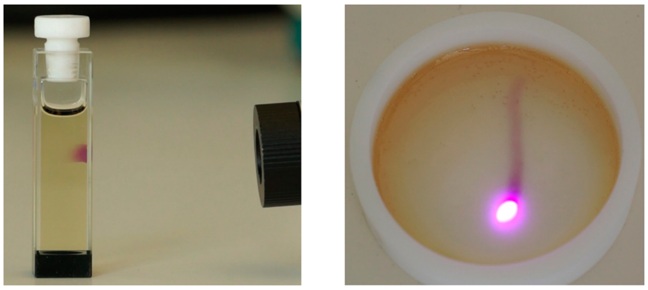

Figure 5. Photos of an irradiated solution of the fused naphthopyran (10^{-3} M in toluene) and an irradiated coating using a high-power laser (405 nm, 200 mW) at 20 °C.

Organic−inorganic matrices are very useful and versatile for the incorporation of photoactive molecules, as their porous structure offers enough free spaces for the reversible structural changes of the photochromic components during photochromic transformations. Their inorganic/organic ratio content can be easily adjusted and their pores functionalized with several organic groups to stabilize/destabilize the open form, thus allowing the color rate decay to be tuned.[12,17] The fused naphthopyran **4** was therefore dispersed in an organic−inorganic hybrid material, following the sol−gel method and using a functionalized silane precursor with one epoxy group ((3-glycidoxypropyl)methyldiethoxysilane, GPTMS) to afford a doped transparent solid yellowish thin film. UV irradiation of this material at room temperature using a high-power laser (405 nm, 200 mW) led to the development of a pink coloration with a half-life time of 80 ms, returning completely to the initial

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uncolored state, in the absence of light, in 280 ms (Figure 5 and video 2 in the Supporting Information). Thus, as the light passes over the material, a pink track is visible in the material, which fades very quickly. This fast color switching is due to the photoisomerization of fused naphthopyran **4** to the TC isomer, which is thermally unstable and fades back to the closed form (Figure 4). The process can be performed several times in the presence of oxygen without noticeable degradation. The fast thermal relaxation of the photogenerated species, within the millisecond time domain, also paves the way for applications in optical data processing[18] and dynamic holographic materials.[19]

Due to the very fast thermal decay, this compound is not activated by sunlight, though the structure manipulation of the molecule, or the matrix, may cause an increase in the stability of the opened form, leading to a color switching system working in the 10−40 °C temperature range under sunlight with the advantage of a quick and complete return to the uncolored state. The synthetic method to obtain this system is very simple, and starting from an unsymmetrical benzophenone, it is possible to obtain, in just three steps, a wide range of naphthopyrans bearing two different aryl groups at the sp^3 carbon atom, which are crucial to obtain a gray coloring and fast switching naphthopyran required by the lens industry.

■ CONCLUSION

The introduction of substituents in the pyran double bond of naphthopyrans does not prevent photochromism, although a significant decrease in the thermal stability of the opened colored forms is observed, thus affording fast switching systems. The introduction of a bridged system between the pyran double bond and the naphthalene core is an efficient strategy to prevent the formation of the short-lived TT isomer. Using a new synthetic approach, with three steps, a new fused naphthopyran with a fast switching between the uncolored and colored form was prepared. UV irradiation of this compound in solution or dispersed in a hybrid matrix at room temperature leads to the opening of the pyran ring with formation of only one colored photoisomer with a short lifetime that bleaches in a few milliseconds to the initial uncolored state. The synthetic strategy developed for this compound allows its structural modification toward a fast gray coloring naphthopyran.

■ EXPERIMENTAL SECTION

General Methods. The reactions were monitored by thin-layer chromatography (TLC) on aluminum plates precoated with silica gel 60 F254 (0.25 mm). Column chromatography was performed on silica gel 60 (70−230 mesh). The new compounds were determined to be >95% pure by ^{1}H NMR spectroscopy. NMR spectra in $CDCl_3$ were recorded at 298 K using spectrometers ($\nu_0(^1H)$ = 300, 400, and 500 MHz). Chemical shifts (δ) are reported in parts per million. IR spectra were obtained using KBr disks (wavenumbers in cm^{-1}). HRMS spectra was recorded on an ESI-TOF mass spectrometer.

1,1-Bis(2-methoxyphenyl)-3-phenylprop-2-yn-1-ol 1. *n*-Butyllithium (10.5 mL, 16.52 mmol, 1.6 M hexanes) was slowly added to a cold (0 °C) solution of phenylacetylene (930 mg, 9.08 mmol) in dry THF (30 mL) and stirred for 1 h. 2,2′-Dimethoxybenzophenone (2.00 g, 8.26 mmol) was added in a single portion to the solution, and the mixture was stirred at room temperature for 22 h and examined by TLC (the reaction was not complete). The solvent was removed at reduced pressure, and NH_4Cl (aq, saturated, 50 mL) was added. The aqueous phase was extracted with ethyl acetate (3 × 75 mL), and the combined organic phases were washed with water (3 × 75 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the product was purified by crystallization with CH_2Cl_2/petroleum ether to give **1** as white crystals (1.821 g; 64%): mp 127.1−130.1 °C; IR (KBr, cm^{-1}) 3482, 3428, 2932, 2838, 1590, 1489, 1456, 1436, 1369, 1281, 1248, 1033, 906, 758, 691, 637, 524; ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 132.0, 131.8, 129.0, 128.1 (two carbons), 128.0, 123.4, 120.5, 112.5, 90.9, 85.2, 73.5, 55.9; ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.79 (dd, *J* = 7.8 Hz, *J* = 1.7 Hz, 2H), 7.46 (m, 2H), 7.28 (m, 5H), 6.97 (td, *J* = 1.0 Hz, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 3.70 (s, 6H, OMe); EI-MS (TOF) *m*/*z* (%) 344 (19), 329 (29), 313 (100), 297 (47), 285 (10), 269 (18), 265 (16), 252 (20), 239 (22), 236 (31) 225 (20), 211 (17), 200 (14), 176 (43), 135 (56); HRMS calcd for $C_{23}H_{20}O_3$ 344.1412, found 344.1411.

5-Oxo-2,2-bis(2-methoxyphenyl)-2*H*-4-phenylindeno[2,3-*f*]naphtho[1,2-*b*]pyran 2. A solution of 5-hydroxy-7*H*-benzo[*c*]fluoren-7-one (500 mg, 2.0 mmol), 3-phenylprop-2-yn-1ol **1** (700 mg; 2.0 mmol), and APTS (catalytic) in toluene (50 mL) was heated under reflux. After 4 h, another equivalent of 3-phenylprop-2-yn-1-ol **1** (700 mg; 2.0 mmol) was added and the mixture maintained under reflux for an additional 2 h. Water (40 mL) was added, and the aqueous phase was extracted with ethyl acetate (3 × 35 mL). The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure, and the residue was crystallized from CH_2Cl_2/$CHCl_3$/petroleum ether to give **2** as red crystals (777 mg; 67%): mp 222.3−226.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (m, 1H), 8.45 (m, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.81 (dd, *J* = 7.9 Hz, *J* = 1.7 Hz, 2H), 7.62 (m, 2H), 7.48−7.25 (m, 7H), 7.19 (td, *J* = 7.6 Hz, *J* = 1.7 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.91 (td, *J* = 7.6 Hz, *J* = 1.0 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 6.49 (s, 1H), 3.59 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 157.1, 151.8, 144.7, 141.8, 136.3, 134.4, 134.2, 133.8, 130.7, 130.3, 129.3, 129.2, 128.8, 128.7, 128.3, 128.1, 128.0, 127.6, 127.4, 126.9, 126.6, 124.6, 123.6, 122.0, 119.8, 115.6, 112.3, 81.6, 55.6; EI-MS (TOF) *m*/*z* (%) 527 (100), 465 (20), 464 (23), 451 (10), 449 (12), 433 (14), 360 (29), 327 (35), 246 (25), 189 (19); HRMS calcd for $C_{40}H_{28}O_4$ 572.1988, found 572.1989.

5-Hydroxy-2,2-bis(2-methoxyphenyl)-2*H*-4,5-diphenylindeno[2,3-*f*]naphtho[1,2-*b*]pyran 3. To a solution of naphthopyran **2** (150 mg, 0.26 mmol) in dry THF (15 mL) at 0 °C was added PhLi (0.582 mL, 1.049 mmol, 1.6 M hexane). After being stirred for 30 min, TLC examination indicated that no naphthopyran remained. Cold water (30 mL) was added, and the aqueous phase was extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with water (6 × 50 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, leaving the crude naphthopyran **3**. The crude product was purified by recrystallization with CH_2Cl_2/petroleum ether to give pink crystals (111 mg, 65%); IR (KBr, cm^{-1}) 3544, 3437, 3065, 2937, 2829, 2357, 1602, 1488, 1461, 1388, 1240, 1106, 1026, 751, 704; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 8.3 Hz, *J* = 1.0 Hz, 1H), 8.67 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.84 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 1H), 7.66 (td, *J* = 6.9 Hz, *J* = 1.6 Hz, 1H), 7.61 (td, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.45 (dd, *J* = 7.9 Hz, *J* = 1.7 Hz, 1H), 7.37 (tt, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H), 7.31 (td, *J* = 7.7 Hz, *J* = 1.1 Hz, 1H), 7.29−7.21 (m, 5H), 7.16 (t, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.08−7.02 (m, 3H), 6.85 (dd, *J* = 8.2 Hz, *J* = 0.8 Hz, 1H), 6.82 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.45 (d, *J* = 7.5 Hz, 1H), 6.08 (s, 1H), 3.58 (s, 3H), 3.49 (s, 3H), 2.09 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 156.6, 150.7, 150.2, 143.8, 143.1, 142.5, 139.0, 134,1, 131.90, 131.88, 130.9, 130.0, 129.9, 129.7, 129.2, 129.0, 128.9, 128.7, 128.5, 128.21, 128.16, 128.0, 127.5, 126.9, 126.3, 125.8, 125.6, 124.3, 124.0, 123.7, 121.9, 120.2, 119.1, 117.7, 112.6, 111.9, 83.5, 80.7, 55.7, 55.2; EI-MS (TOF) *m*/*z* (%) 650 (6), 635 (30), 634 (100), 527 (10), 422 (9), 376 (8), 181 (17); HRMS calcd for $C_{46}H_{34}O_4$ 650.2457, found 650.2446.

2,2-Bis(2-methoxyphenyl)-8-phenyl-2*H*-8*H*-benzo[3,4]fluoreno[2,1,9-*def*]nafto[1,2-*b*]pyran 4. TFA (1 mL) was added to the crude naphthopyran **3**, and the solution acquired immediately an intense green coloration. The mixture was added to cold water (30 mL) and extracted with ethyl acetate (3 × 25 mL). The organic phase was washed with water (10 × 50 mL), dried (Na_2SO_4), and concentrated under reduced pressure to leave an oil, which was purified by crystallization (CH_2Cl_2/petroleum ether) to give **4** as slightly green crystals (132 mg, 40%): IR (KBr, cm^{-1}) 3443, 3061, 2934, 1574, 1487, 1453, 1239, 1017, 743, 669; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.61 (d, J = 8.3 Hz, 1H), 8.55 (dd, J = 8.3 Hz, J = 1.0 Hz, 1H), 8.29 (dd, J = 7.7 Hz, J = 1.1 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 7.7 Hz, 2H), 7.91 (dd, J = 7.7 Hz, J = 1.2 Hz, 1H), 7.65 (td, J = 6.9 Hz, J = 1.5 Hz, 1H), 7.55 (td, J = 8.0 Hz, J = 1.1 Hz, 1H), 7.45 (td, J = 7.4 Hz, J = 1.3 Hz, 1H), 7.44 (td, J = 7.6 Hz, J = 1.2 Hz, 1H), 7.38−7.26 (m, 4H), 7.11 (td, J = 7.8 Hz, J = 1.1 Hz, 1H), 7.06 (td, J = 8.2 Hz, J = 1.8 Hz, 1H), 7.04−6.91 (m, 4H), 6.75−6.67 (m, 3H), 6.63 (s, 1H), 6.47 (td, J = 7.6 Hz, J = 1.1 Hz, 1H), 3.51 (s, 3H), 3.50 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 158.0, 156.1, 150.0, 148.0, 146.6, 144.8, 142.8, 138.6, 133.1, 132.9, 130.5, 130.4, 130.1, 128.7, 128.6, 128.3, 128.0, 127.7, 127.6, 127.2, 126.9, 126.6, 126.5, 125.8, 125.2, 125.14, 125.06, 124.9, 124.4, 124.1, 123.9, 122.3, 120.4, 119.4, 118.8, 114.0, 112.7, 83.6, 57.5, 55.8, 55.7; EI-MS (TOF) m/z (%) 632 (74), 526 (23, 525 (100), 524 (57), 448 (40), 433 (18), 432 (29), 376 (11); HRMS calcd for $C_{46}H_{32}O_3$ 632.2351, found 632.2355.

Preparation of the Photochromic Organic−Inorganic Hybrid Thin Film. A solution of 3-(glycidoxypropyl)methyldiethoxysilane (1.615 g) in ethanol (1.518 g) was vigorously stirred for 15 min. Next, water (0.468 g) and a catalytic amount of nitric acid (2 drops) were added. The molar ratio of this new mixture is 1/4/4 (GPTMS/EtOH/H_2O). The sol was stirred at ambient temperature for 1.5 h, and then a solution of the fused naphthopyran **4** (8 mg) in THF (0.568 g) was added and the solution stirred vigorously. After 30 min, the sol was deposited in a Teflon Petri dish and subjected to a thermal treatment at 50 °C for 24 h.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02116.

NMR spectra of all new compounds, with proton and carbon assignments for compounds **2**−**4**, NMR characterization of the colored opened photoisomer, and kinetic data (PDF)

Video 1 of the UV irradiation of the fused naphthopyran **4** in solution (AVI)

Video 2 of the UV irradiation of the fused naphthopyran **4** in a hybrid siloxane matrix (AVI)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pcoelho@utad.pt.

Notes

The authors declare no competing financial interest.

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