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Oligothiophene-Linked Bisnaphthopyrans: Sequential and Temperature-Dependent Photochromism

Weili Zhao and Erick M. Carreira*[a]

Abstract: Photochromic bisnaphthopyrans linked with oligothiophenes were synthesized and their photochromic behavior studied. Sequential and temperature-dependent photochromism was observed in the oligothiophene linked bisnaphthopyrans. The kinetics of photo and thermal processes in bisnaphthopyrans in comparison with naphthopyrans were studied. Substituent and linking effects on the photochromic properties are discussed. We demonstrate that the cross-talk between the two photochromophores is dependent on the length of the oligothiophene linker. The presence of the bithiophene linker led to high colorability and high quantum yield of coloration.

Keywords: dyes/pigments · heterocycles · oligothiphene · photochromism · sensors

Introduction

Over the last number of decades, photochromic dyes have attracted considerable attention because of the wide range of potential applications.[1,2] Recent interests have been focused on design, synthesis, and study of novel bisphotochromophores.[3–10] We have recently documented the first bisnaphthopyran showing sequential photochromism wherein the color hue changes with time at room temperature under UV irradiation.[9] In our continuing interest in the discovery of bisphotochromophores displaying novel properties, we have identified bisnaphthopyran systems which display temperature-dependent photochromism. In this paper, we report the detailed synthesis, photochromic behavior, and mechanistic studies of such bisnaphthopyrans linked through oligothiophene spacers.

Among the known bisphotochromic systems reported,[3–10] only a few exhibit behavior that differs significantly from the monomeric counterpart. Studies of covalently-linked interactive photochromophores have been observed only in a few cases involving diarylethene and bisbenzodihydropyrene under continuous irradiation,[3g–l,4] and in dihydroindolizine under laser-induced photolysis.[7b] However, in the former cases, the photogenerated colored form of the diarylethene is thermally stable and fails to undergo fading; and the bisbenzodihydropyrene photochromophore examined displayed inverse photochromism. In the case of dihydroindolizine, the observations made under laser-induced photolysis were not carried over under continuous irradiation. None of the above-mentioned systems are therefore satisfactory for use in protective eye wear or in displays.

A number of bisnaphthopyran systems have been reported, wherein naphthalene subunits are linked via ethenes; however, these display unwanted irreversible photoreactions.[8c] When acetylenic linkages are employed either normal photochromism or no photochromism is observed.[8b,e] Tetrathiafulvalene (TTF)-containing bisnaphthopyrans display weak photochromism.[8j] The use of flexible linkers for the pyrans or, alternatively, fusion of both these units onto a common naphthalene unit fails to lead to novel photochromism.[8g–i] Recently, bis-[3*H*]-naphtho[2,1-*b*]pyrans linked at the sp^3-hybridized carbon of the pyrans with terthiophene or quaterthiophene were reported;[10] however, no kinetic parameters were documented for these systems. Such terthiophene and quaterthiophene linked bisnaphthopyrans are expected to have low photoconversion because of fast fading rate due to the substitution by the electron rich units employed, as well as inherent fluorescence of the oligothiophene linker.[8b]

We have chosen to synthesize and investigate molecules wherein two pyran units are linked through an electron rich bithiophene linker, which is known to afford systems displaying high colorability.[11] In this respect, we have been interested in the influence of linker size on the photochemical properties of bisnaphthopyrans. Implementation of the plan of study has led to the synthesis of **1a**–**h** (see below), which,

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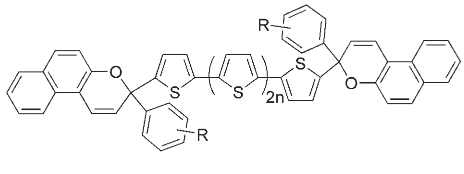
[a] Dr. W. Zhao, Prof. Dr. E. M. Carreira
Laboratorium für Organische Chemie, ETH Zürich, HCI H335
8093 Zürich (Schweiz)
Fax: (+41) 1-632-1328
E-mail: carreira@org.chem.ethz.ch



1a : R = *o*-F, *n* = 0
1b : R = *p*-F, *n* = 0
1c : R = H, *n* = 0
1d : R = *p*-Me, *n* = 0
1e : R = *p*-MeO, *n* = 0
1f : R = *o*-F, *n* = 1
1g : R = β–naphthyl, *n* = 1
1h : R = *p*-MeO, *n* = 1

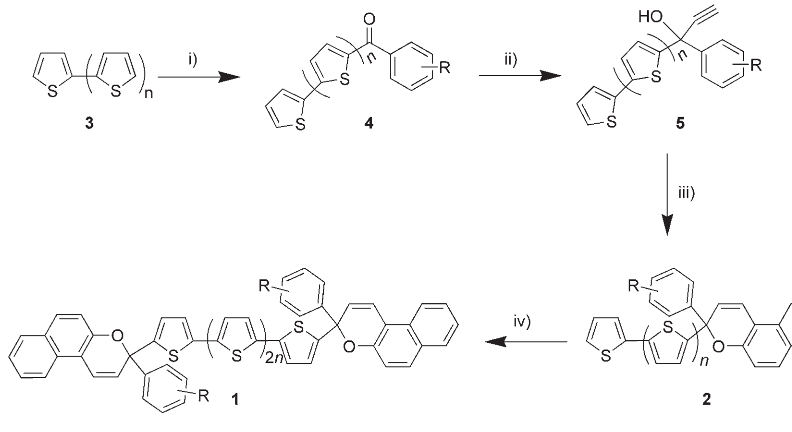
as detailed below, furnishes novel systems wherein covalently coupled photochromophores work synergistically.

Results and Discussion

Synthesis of bisnaphthopyran 1a–h: The approach which has been employed for the preparation of bisnaphthopyrans, such as **1h**, has been to couple 5,5′-bis-trimethyltin-2,2′-bisthiophene and the corresponding substituted 2-(4-bromothienyl)-[3*H*]-naphtho[2,1-*b*]pyrans via Stille cross-coupling.[10a,12] The low yield (43 %) and the use of the distannyl bithiophene detract from the appeal of such a method. The attempted synthesis of bisnaphthopyrans via copper promoted homo-coupling of bromothienyl pyran was unsuccessful.[10a] We have developed a complementary approach to the coupling of naphthopyrans involving the lithiation of the terminal thiophene followed by a copper-promoted homo-coupling (see **2** → **1**, Scheme 1).

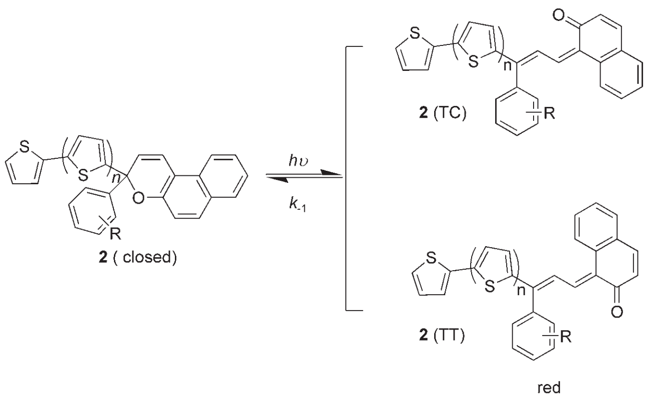
The most commonly used method for preparation of naphthopyrans is based on the Claisen rearrangement of propargyl naphthol ethers, which can be made in situ from naphthol with diaryl propargylic alcohol in the presence of catalytic amounts of acid catalyst (typically, TsOH) in an apolar solvent such as toluene.[13] We recently reported a facile one-pot synthesis of naphthopyrans using pyridinium *p*-toluenesulfonate (PPTS) as the catalyst in combination with trimethyl orthoformate as dehydrating agent.[14] The application of this methodology to the preparation of thiophene substituted naphthopyran compounds affords **2a–i** in excellent yields. The starting aromatic thienyl ketones were synthesized by Friedel-Crafts reaction of thiophene precursor **3** with aroyl chloride in dry CH_2Cl_2 by using tin tetrachloride as catalyst, which afforded the desired ketones **4a–i** in good to excellent yields. The required 3,3-disubstituted propargyl alcohols **5a–i** were synthesized from aromatic ketones by reaction with sodium acetylide. We noted that the use of excess acetylene gas in the reaction mixture through its continuous bubbling is helpful in reducing the amount of side product (2-butyne-1,4-diol derivative) resulting from double addition.[15] This protocol represents a useful improvement to the preparation of these building blocks. Thus, although **5h** was reported in yield of 36 % using 3 equiv of sodium acetylide in xylene,[16] it could be prepared in yield of 71 % by using only 1.68 equiv of sodium acetylide with this modified procedure.[14] The homo-coupling reaction of thienyl naphthopyran was performed in THF with the lithiated species at low temperature using cupric chloride (1.6–2.0 equiv) as oxidant. Good to excellent yields (55–97 %) of bisnaphthopyrans were obtained from various thienyl naphthopyrans.

Due to the symmetric nature of bisnaphthopyrans **1a–h**, the ^{1}H NMR spectra are relatively simple. The characteristic ^{1}H NMR resonance for the vinyl proton adjacent to the carbon bearing the heteroatom (O) for **1c–e** and **1g–h** (the non-fluorinated compounds) can be found as doublets at δ 6.0–6.3 ppm with a coupling constant of 10 Hz. The ^{13}C NMR of the sp^3-hybridized carbon is also characteristic, appearing at about 80 ppm. In the case of fluorine substituted bisnaphthopyrans, coupling patterns are consistent with those reported for similarly-substituted fluorinated pyrans.[8f] For example, the vinyl proton adjacent to the heteroatom in the *ortho*-fluorophenyl substituted bisnaphthopyran **1a** appears as a doublet of doublets in the ^{1}H NMR spectrum due to $^5J_{H,F}$ coupling and as a doublet in the ^{13}C NMR spectrum due to $^5J_{C,F}$ coupling.[8f]



Scheme 1. Synthesis of bisnaphthopyran **1**. i) acyl chloride (1.04 equiv), $SnCl_4$ (1.04 equiv), CH_2Cl_2, −4 to 23 °C: **4a**, 98.0 %; **4b**, 91.1 %; **4c**, 89.6 %; **4d**, 92.6 %; **4e**, 98.0 %; **4f**, 44.5 %; **4g**, 62.0 %; **4h**, 67.7 %; **4i**, 57.8 %; ii) sodium acetylide (1.4–2.0 equiv), DMSO, acetylene, 2–3 h, 23 °C: **5a**, 60.2 %; **5b**, 82.4 %; **5c**,[17] 74.5 %; **5d**, 86.6 %; **5e**, 84.1 %; **5f**, 82.7 %; **5g**, 86.6 %; **5h**, 71.0 %; **5i**, 82.7 %; iii) 2-naphthol (1.0 equiv), PPTS (5 mmol %), 23 °C to reflux, $(CH_2Cl)_2$: **2a**, 88.8 %; **2b**, 98.2 %; **2c**, 97.0 %; **2d**, 95.3 %; **2e**, 92.0 %; **2f**, 89.2 %; **2g**, 92.4 %; **2h**, 83.5 %; **2i**, 94.5 %; iv) *n*Buli (1.6 M, 1.6 equiv), $CuCl_2$ (1.6–2.0 equiv), −78 to 23 °C, overnight: **1a**, 72.7 %; **1b**, 55.0 %; **1c**, 96.5 %; **1d**, 77.1 %; **1e**, 65.5 %; **1f**, 76.9 %; **1g**, 88.2 %; **1h**, 83.5 %.

Photochromism of bithiophene linked bisnaphthopyran 1a–e in solutions: All of the bisnaphthopyrans **1a–h** synthesized in this study as well as their precursors (**2a–i**) are photochromic. The mechanistic details of the photochromism of the monomeric precursor pyran **2** are shown in Scheme 2. It is well-known that the original state of compound **2** is the closed pyran form (closed). Upon exposure to UV irradiation, the colored species generated are the more abundant and fast-fading *trans–cis* (TC) and the *trans–trans* (TT), which is present as a minor component and is most stable.[12] The TC form has been shown to be generated preferentially in the early stages of the photocoloration process.[18] These (TC and TT) can undergo thermal fading, and the bleaching process can be enhanced photochemically with visible light.



Scheme 2. Photochromic reaction of pyran **2**.

The color change and UV spectra of photochromophoric bispyran **1a** upon UV irradiation in toluene at room temperature are shown in Figure 1. The near colorless solution of **1a** (2.5×10^{-5} M in toluene) rapidly undergoes coloration to orange-red after irradiation with UV (366 nm) for 5 s. Exposure of **1a** for extended periods of time produced interesting results. The color hue changed to red-purple after 30 s and to purple-blue after 4 min. Removal of the irradiation source resulted in fading of the color in the reverse order. After 30 min a residual color persists (pale red), which fades slowly; however, it is susceptible to rapid bleaching upon irradiation with visible light.

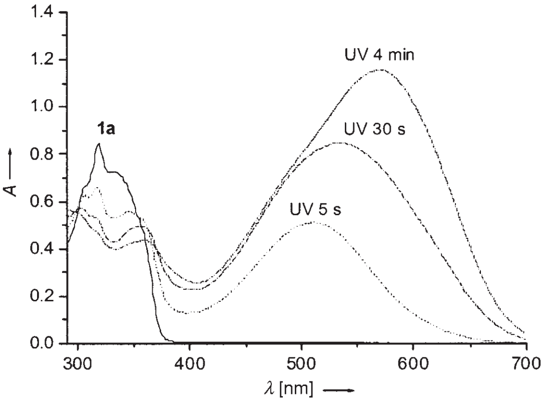


Figure 1. UV-visible spectra of compound **1a** (2.5×10^{-5} M in toluene) prior to and after UV (366 nm) irradiation for 5, 30 s and 4 min at room temperature.

Compound **1a** has absorption maxima (λ, in nm) and extinction coefficients (ε, in $\mathrm{mol^{-1}dm^{3}cm^{-1}}$) at 306 (sh) (26700), 318 (33800), 333 (sh) (28400), which are similar to the absorption maxima displayed by bithiophene **2f** [306 (sh) (20700), 317 (23400)] but with larger extinction coefficients. Monothiophene **2a** [304 (5520), 316 (6400), 346 (4360), and 358 (4200)] has quite different absorption from either **1a** or **2f** (see Figure 2). By comparing Figure 1 and 2, it is clear that bithiophene linked bisnaphthopyran **1a** has greater similarity to compound **2f** with a bithiophene substituent than to monothiophene **2a**. Upon exposure to UV light, the absorption maxima remain almost unchanged following UV irradiation for 5 s and 2 min, respectively, for both **2a** and **2f**.

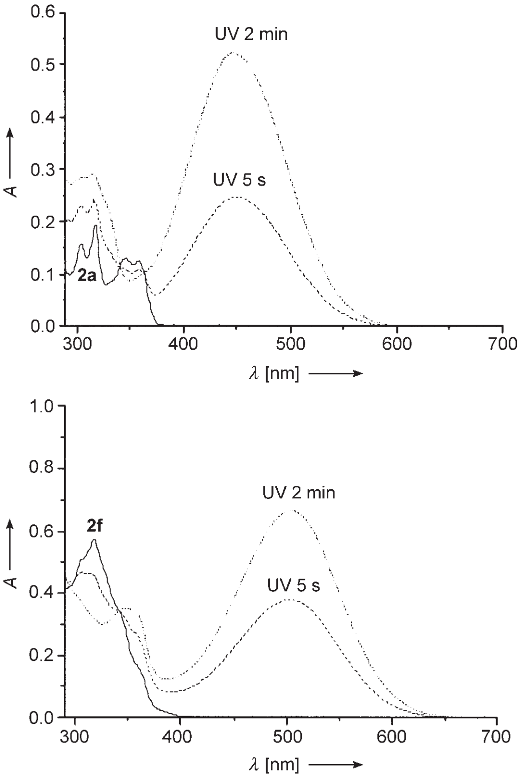


Figure 2. UV-visible spectra of compound **2a** (top) and **2f** (bottom) (both 2.5×10^{-5} M in toluene) prior to and after UV (366 nm) irradiation for 5 s and 2 min at room temperature.

The dramatic change of color hue of bisnaphthopyran **1a** upon extended periods of irradiation with UV light suggests that a sequential photochromic process has taken place in **1a**, namely ring-opening and coloration of the second naphthopyran unit takes place following the opening of the first naphthopyran unit upon extended irradiation. In contrast to **1a**, no sequential photochromism was observed for **1b** at room temperature. When a solution of compound **1b** in toluene was irradiated with UV (366 nm) at ambient temperature, the colorless solution turned to red rapidly, however, no change of color hue was observed under prolonged (even intense) irradiation, which suggests that the position of fluorine substituent plays important role in the photochromic behavior of bisnaphthopyran **1a**/**1b**.

It is known that *ortho*-fluoro substitution slows down the fading rate dramatically compared with *para*-fluoro substitution in photochromic pyran systems.[13] The main difference between **1a** and **1b** is that the thermal fading in **1a** is slow, however in **1b** is fast. We speculated that by lowering the temperature to slow down the fading process, sequential photochromism would then be observed in **1b**. Consistent with this hypothesis, when a cold solution of **1b** was irradiated with UV light, the colorless solution changed to purple (5 °C) and to purple-blue (−10 °C) gradually (see Figure 3).

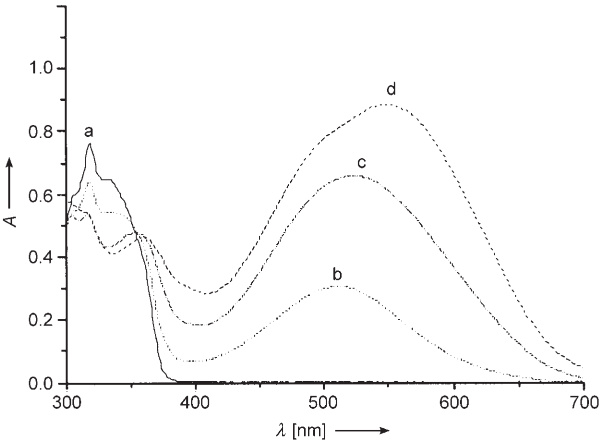


Figure 3. UV/Vis spectra of compound **1b** (2.3×10^{-5} M in toluene) prior to and after UV (366 nm) irradiation for 4 min at various temperature. a) Prior to UV irradiation; b) UV irradiation at ambient temperature; c) UV irradiation at 5 °C; d) UV irradiation at −10 °C.

For comparison, the color hue of reference compound **2i** upon UV irradiation remains unchanged in the same range of temperature, and only an increase in intensity of the color was observed. For **1b** in the dark, the color faded through the color sequence observed during coloration, but in reverse. Thus **1b** displays interesting temperature-dependent photochromism.

Temperature-dependent photochromism had been observed in spiropyran systems bearing a spiroindoline ring at the sp^3-hybridized carbon adjacent to a pyran oxygen at very low temperature (≤ -80 °C). This has been attributed to the thermal equilibration between various colored species generated from the same photochromophore, as well as to aggregates of the colored forms.[19] A noteworthy difference between the spiroindolinepyran and pyran photochromophores is that the pyran system generates a quinoid in its open form whereas the spiropyran is transformed into a zwitterionic open form.[1,13] In our dimeric pyran system, we believe that the mechanism of temperature-dependent photochromism is completely different from the spiropyran due to the opening of the second photochromic unit in the bispyran molecule **1b**. The discovery of sequential photochromism in **1a** and temperature-dependent photochromism in **1b** prompted us to investigate the photochromism of these bisnaphthopyrans in quantitative manner.

A number of mathematical approximations and simulations have to be used for the kinetic study of photochromic pyrans wherein the reversible thermal and photochemical processes involve more than two colored species.[20,21] Additional difficulties are expected for the kinetic study with bisnaphthopyrans **1a**/**1b** as a consequence of the two photochromic units present in the same molecule.

We proceeded to identify the colored species generated with **1a** after UV irradiation. In prior work, it has been demonstrated that the fast fading colored species (**TC**) of 2,2-di(4-fluorophenyl)-6-methoxy-2*H*-1-chromene generated by UV irradiation has half life time ($t_{1/2}$) about 1.5 h at −45 °C.[22] With this background information in hand, we proceeded to isolate the various colored intermediates generated by UV irradiation through the use of low-temperature chromatography (−78 °C).

Chromatographic separation at low temperature was first applied to the known 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyran as a control experiment in order to check the validity and feasibility of the method for the separation of unstable colored species. We managed to isolate two colored species: one during the early stage of irradiation, which is assigned to the TC form and a second minor, which is more stable, and thus assigned to the TT form. The isolated TC form has ε value of 18100 $mol^{-1} dm^3 cm^{-1}$ at the absorption maximum, and the isolated TT form displays ε = 16900 $mol^{-1} dm^3 cm^{-1}$. The former is in good agreement to the previously reported simulation data, while the latter is not. However, as noted in the earlier simulation work,[20a] the large error associated with the predicted value for the miniscule amounts the TT form casts into question the accuracy of this value.

Upon irradiation of **1a**, two red and one purple-blue species could be identified. Three different separation strategies were employed in order to isolate and examine these individually. For the separation of the fast-fading red compound with absorption at 517 nm at ambient temperature, a solution of **1a** was irradiated at 366 nm for 5 s at −30 °C in CH_2Cl_2/hexane 2:1 and then transferred to a column of silica gel at −78 °C. Elution initially with cold CH_2Cl_2 followed by CH_2Cl_2/Et_2O 100:1 under slight vacuum permitted the collection of various fractions into thick-walled tubes which were immersed in liquid nitrogen. These fractions were then transferred to a pre-cooled cuvette in an Oxford Cryostat; as the frozen fractions partially melted, the UV/Vis spectrum was acquired at −78 °C. The colored solution isolated was allowed to warm up to room temperature and was kept in dark until complete fading of the color had been observed. The absorption spectrum of bisnaphthopyran **1a** that had been isolated through the procedure described was compared to a standard solution of **1a**. In such manner the concentration of the isolated colored form could be determined. The spectrum of isolated colored form (red, fast fading) of **1a** has the same shape as the one generated at room temperature by exposure to UV irradiation for 5 s. The intensity of the spectrum taken at room temperature was 85 % intensity of the one taken at −78 °C due to the change of the volume of the solvent. Thus the extinction coefficient of the isolated colored form (converted to the value at room temperature) could be calculated according to Lambert–Beer law to be 303 (27200), 317 (24600), 358 (21900), 514 (29200).

For separation of the more stable red species present in minor quantities generated from **1a**, it was exposed to UV (366 nm) for an extended period of time. A solution of compound **1a** in CH_2Cl_2/hexane 2:1 was initially irradiated with UV (366 nm) for 50 s at 20 °C and was allowed to fade at room temperature so as to eliminate the fast fading red species as monitored with a Cary 50 UV/Vis spectrometer at 510 nm. The partially faded solution of **1a** was resubmitted to another cycle of irradiation along with fading as described above, and then the colored solution was loaded on a pre-cooled column (−78 °C) of silica gel. Elution with cold CH_2Cl_2 followed by CH_2Cl_2/Et_2O 100:1 under slight vacuum permitted the collection of various fractions into thick-walled tubes which were immersed in liquid nitrogen and treated as described for the fast-fading red species. The extinction coefficient of the isolated red species displaying slow fading rate was calculated to be 303 (19000), 317 (19700), 360 (19400), 523 (25200) at room temperature.

For the separation of the purple-blue colored species, **1a** in CH_2Cl_2/hexane 2:1 was irradiated with UV (366 nm) for 4 min at −30 °C, and the chromatographic separation was effected following a similar protocol. The extinction coefficient of the isolated purple-blue species with slow fading rate was calculated to be 282 (26300), 370 (17700), 500sh (26900), 593 (47800). The spectra of isolated colored species of **1a** at −78 °C are superimposed and shown in Figure 4.

Compound **1b** displayed the same number of colored species at low temperature. The protocol for the isolation of these colored species of **1b** was identical to that detailed for **1a**. The spectra of isolated colored species of **1b** are shown in Figure 5. The spectroscopic data for **1a** and **b** as well as reference compounds **2f** and **i** are collected in Table 1.

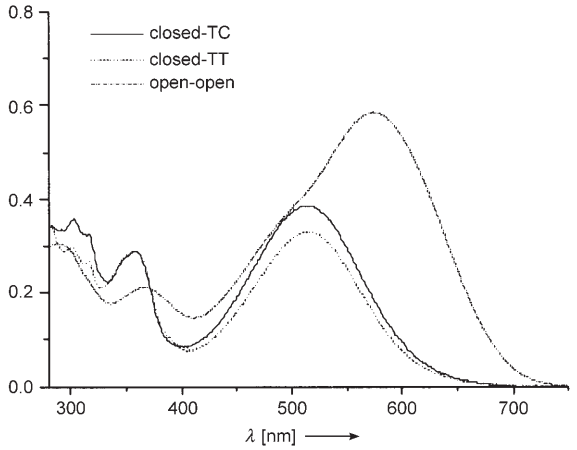


Figure 4. Absorption spectra of the colored species of **1a** isolated by low-temperature chromatography on silica gel at −78 °C in CH_2Cl_2/Et_2O 100:1.

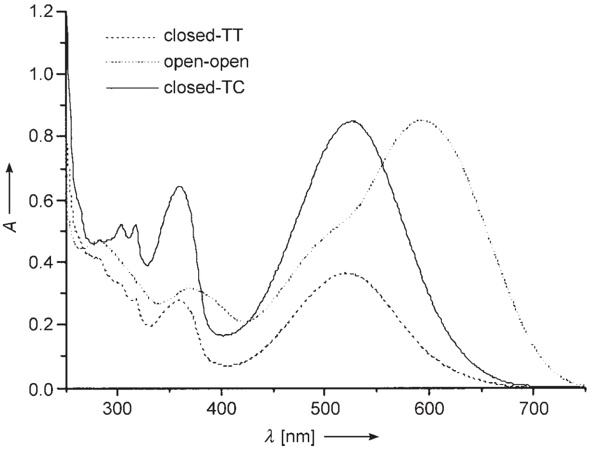


Figure 5. Absorption spectra of the colored species generated from **1b** isolated by low-temperature chromatography on silica gel at −78 °C in CH_2Cl_2/Et_2O 100:1.

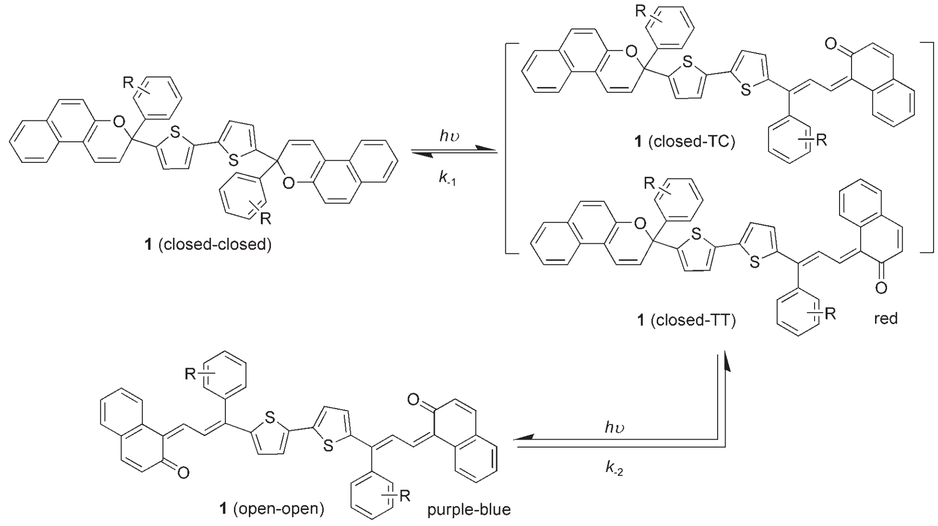
Table 1. Spectroscopic data of bisnaphthopyrans and reference pyrans in CH_2Cl_2 as well as their colored forms in CH_2Cl_2/Et_2O 100:1. ε is in the unit of $mol^{-1}dm^3cm^{-1}$.

Compound	ε[a] closed–closed	ε closed-TC	ε closed-TT	ε open–open
1a	306sh (26800) 318 (33800) 333sh (28100)	303 (27200) 317 (24600) 358 (21900) 514 (29200)	303 (21200) 316 (18700) 359 (21100) 514 (23900)	289 (22000) 366 (15400) 574 (42200)
1b	306sh (26200) 318 (33200) 333sh (28000)	303 (17700) 317 (17800) 360 (22000) 527 (29000)	303 (19000) 317 (19700) 360 (19400) 523 (25200)	282 (26300) 370 (17700) 500sh (26900) 593 (47800)

Compound	ε* closed	ε TC	ε TT
2f	306sh (20700) 317 (23300)	295 (17400) 358 (13100) 506 (24000)	283 (19900) 356 (14900) 512 (19000)
2i	306sh (21300) 317 (23900)	302 (18200) 364 (16000) 518 (26800)	362 (15800) 521 (25800)

[a] In CH_2Cl_2.

The coloration behavior of bisnaphthopyrans **1c–e** is similar to that of **1b**. The photochromic mechanism of **1a–e** is shown in Scheme 3. On the basis of prior work in this area, it is reasonable to attribute the fast-fading red species to the s-*trans–cis* forms (only one isomer of the two is shown as closed-TC); the red species generated with slow thermal fading rate can be assigned to the s-*trans–trans* forms (only one isomer of the two is shown as closed-TT). The purple-blue species results from further irradiation and is generated upon opening of both pyran units to a form with extended conjugation (only one isomer is shown as open–open).



Scheme 3. Photochromic reaction of bisnaphthopyran **1a–e**.

With the data presented, the quantum yield for the generation of the fast-fading red species can be calculated. In general at an early stage of the photocoloration reaction, we speculate that closed-TC was formed preferentially upon exposure to UV, as has been claimed in photochromic pyrans.[18] This allows simplification of the photochromic sequence, which can then be described with the accompanying equation: closed–closed $\underset{k_{-1}}{\overset{\Phi}{\rightleftharpoons}}$ closed-TC $\mathrm{d}A_{\text{closed-TC}}/\mathrm{d}t = \varepsilon_{\text{closed-TC}}\Phi I_0[1-\exp(-2.3A_{\text{closed–closed}})] - k_{-1}A_{\text{closed-TC}}$.[20b,21]

The maximum absorbance of closed-TC is defined by $A_{\text{closed-TC}}$. The extinction coefficient of closed-TC ($\varepsilon_{\text{closed-TC}}$) is collected in Table 1; Φ corresponds to the quantum yield of the photoreaction. I_0 is defined as the intensity of the incident light. Similarly, $A_{\text{closed–closed}}$ is the absorbance of closed–closed at the irradiation wavelength (366 nm). By plotting $\mathrm{d}A_{\text{closed-TC}}/\mathrm{d}t$ versus $A_{\text{closed–closed}}$ and extrapolating the color-forming rate to zero time, the quantum yield Φ could be calculated using: $\Phi = (\mathrm{d}A_{\text{closed-TC}}/\mathrm{d}t)_{t\to 0}/\{\varepsilon_{\text{closed-TC}}I_0[1-\exp(-2.3A_{\text{closed–closed}})]\}$.

Photocoloration was performed with a 50 μM solution of photochromic compounds in a thermostated quartz cuvette irradiated with UV (366 nm) at a 90° angle to the monitoring beam and was monitored at absorption maxima of the colored forms with a Cary 50 UV/Vis spectrometer. I_0 was measured by the standard procedure using potassium ferrioxalate actinometer to be 4.99×10^{-6} Einstein $\mathrm{s}^{-1}\,\mathrm{dm}^{-3}$.[23] Under irradiation with 366 nm light, $A_{\text{closed–closed}} = 0.437$ for **1b**. The absorbance at 527 nm for 50 μM solution of **1b** in CH_2Cl_2 upon UV irradiation at 300 K is shown in Figure 6a. We assume that the small differences (3 nm) in the absorption maxima at room temperature from the one at −78 °C will not affect the value of ε. We also noted that there is no difference of the absorbance of photochromic compounds in CH_2Cl_2 from the one in CH_2Cl_2/Et_2O 100:1 so that we could directly use the ε value from Table 1 for the calculations. $(\mathrm{d}A_{\text{closed-TC}}/\mathrm{d}t)_{t\to 0}$ could be obtained from a linear fitting of photocoloration shown in Figure 6b. When the change of absorbance ($\mathrm{d}A_{\text{closed-TC}}/\mathrm{d}t$) was plotted against absorbance A,

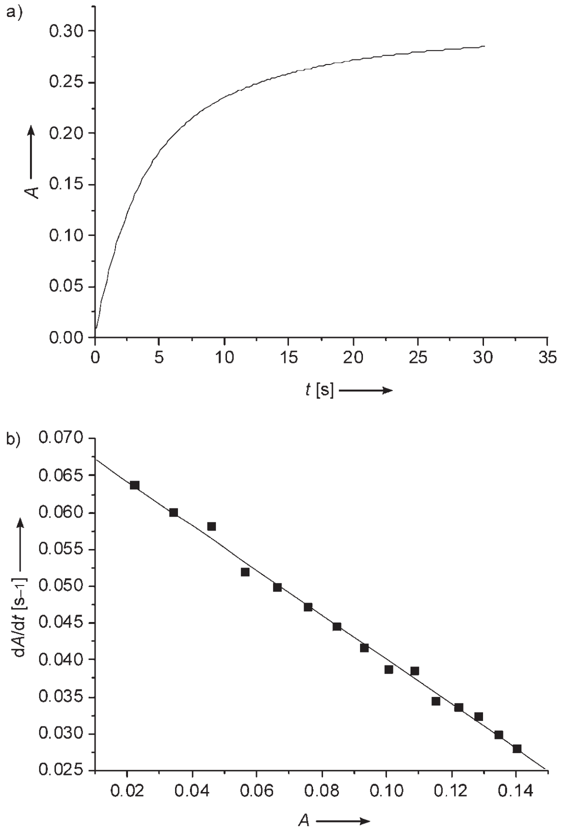


Figure 6. Photocoloration of compound **1b** in CH_2Cl_2 (5×10^{-5} M) at 300 K. a) Absorbance of closed-TC at 515 nm upon UV irradiation; b) experimental data treated according to Equation (1).

very good linear relationship with a correlation coefficient better than 0.99 was obtained. Thus $(dA_{\text{closed-TC}}/dt)_{t\rightarrow 0}$ was calculated to be 0.070. Repetition of three parallel measurements allowed the determination of Φ as 0.76 ± 0.01.

We next proceeded to determine the fading rate of the fast-fading red species. Upon removal of the irradiation source, the thermal fading process could be followed with a Cary 50 UV/Vis spectrometer. In general, in this field biexponential fading processes are involved for these processes. Upon short irradiation (t = 6 s), due to the low content of slow fading closed-TT, the fading process is dominated by closed-TC and could be simplified and represented as a monoexponential process. The fading of color monitored at 527 nm at 298.4 K for a 50 μM solution of **1b** in CH_2Cl_2 after 5 s of UV (366 nm) irradiation is shown in Figure 7a. Mathematic manipulation of the curve in Figure 7a by plotting dA/dt versus time leads to good linearity (correlation coefficient better than 0.99) and the rate of thermal fading for closed-TC was calculated to be $0.165\ s^{-1}$ at 298.4 K. By measuring fading rate at various temperatures, the activation energy (E_a) of thermal fading of closed-TC for **1b** could be obtained from Arrhenius plots as shown in Figure 7b and was calculated to be $56.95\ kJ\,mol^{-1}$.

In a similar fashion, the coloration and thermal fading for all other bispyrans as well as for reference compounds **2f** and **i** were also measured. The data obtained are collected in Table 2.

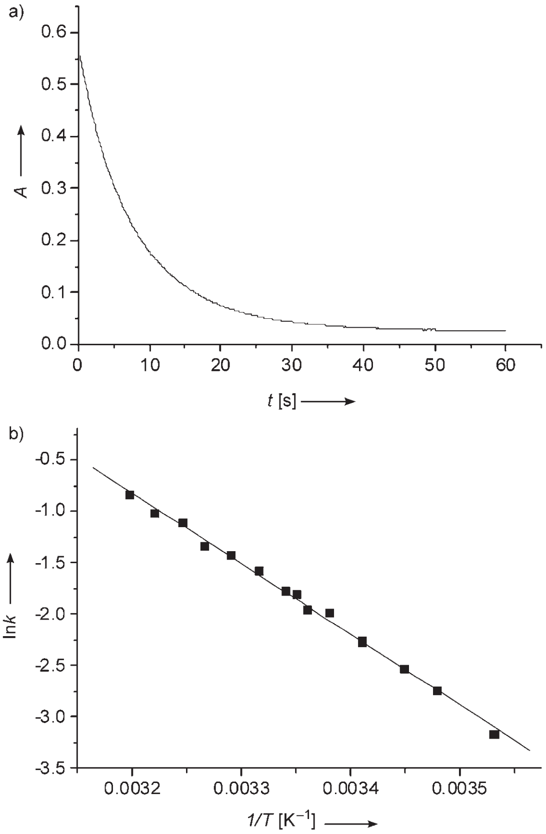


Figure 7. a) Thermal bleaching of the colored species of compound **1b** at 298 K after UV activation; b) Arrhenius plots of the kinetic parameters of closed-TC.

Table 2. Kinetic parameters of bisnaphthopyran **1a**–**e** and reference compound **2f**, and **2i** in CH_2Cl_2.

Compound	Φ (300 K)	k_{-1} [s^{-1}] (298.4 K)	E_a [$kJ\,mol^{-1}$]
1a	0.72	0.0405	60.93
1b	0.76	0.151	56.95
1c	0.95	0.126	–[a]
1d	–[a]	0.171	–[a]
1e	–[a]	0.278	–[a]
2f	0.76	0.0382	64.11
2i	0.81	0.167	56.30

[a] Not measured.

The photochromic bispyrans **1a**–**e** display similar kinetics for both photocoloration and fading to that observed for reference compound **2** (**1a** versus **2f** and **1b** versus **2i**) with same substitution pattern. Bithiophene-linked bispyrans **1a**–**e** and bithiophene-substituted pyrans **2f** and **2i** all have very efficient photocoloration processes. The thermal fading rate is dependent on the substitution pattern. In **1a** and reference **2f**, the *ortho*-fluoro substituent leads to high energy barrier and slow fading. The unsubstituted or *para*-substituted pyran systems along with the bispyran **1b**–**e** display fast fading, which is promoted by substitution with electron-donating groups.

The extinction coefficients for **1a**–**e** in CH_2Cl_2 and in toluene fall within a narrow range. For example for compound **1a**, the extinction coefficients in toluene are: 306sh (25700), 318 (32900), 333sh (28300), which are very close to the values in CH_2Cl_2. Assuming the ε value of the colored species does not change in CH_2Cl_2 and in toluene, we could estimate the quantum yield (300 K) for photocoloration of bisnaphthopyrans in toluene: **1a**, 0.76; **1b**, 0.76; **1c**, 0.97; **2f**, 0.81; **2i**, 0.82.

We next conducted a study of the fluorescence of the bithiophene-linked bisnaphthopyrans, in order to gain insight into the novel properties of bisnaphthopyran **1a**–**e**. In general, for bisphotochromophores, only one photochromic unit operates in most cases. Irie et al. attributed the failure of operation of the second photochromic unit in dimeric diarylethene systems to intramolecular energy transfer.[3e] In our bisnaphthopyran systems, we observed clearly the sequential photochromism in **1a** at room temperature and in **1b**–**e** at low temperature.

The absorption and fluorescence spectra of **1a** are shown in Figure 8. Very weak fluorescence of **1a** was observed with quantum yield estimated to be only 0.00013 by using 9,10-diphenylanthracene as the standard.[24] The colored species formed from **1a** (closed-TC, closed-TT, and open–open) do not show any detectable fluorescence at room temperature, which suggests that intramolecular energy transfer does not seem to occur from the colored forms of **1a**. Consequently, the high reaction quantum yield and lack of efficient intramolecular energy transfer pathway may probably explain the sequential photochromism in **1a**.

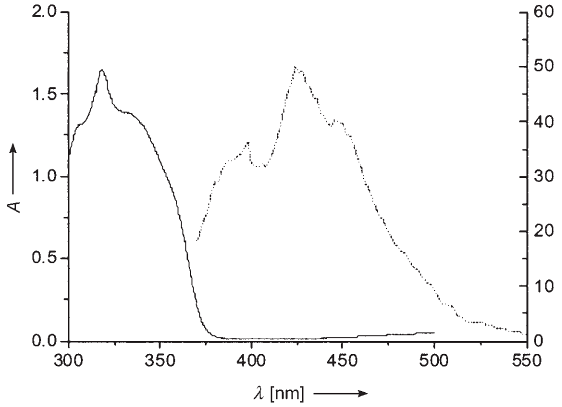


Figure 8. Absorption spectra of bisnaphthopyran **1a** (5.0×10^{-5} M) and fluorescence spectra of **1a** ($A=0.04$ at 353 nm) in chloroform at room temperature.

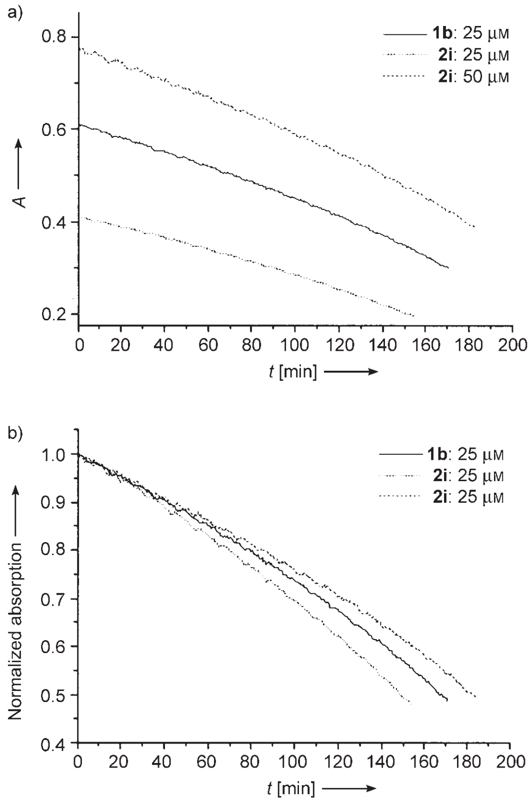


Figure 9. Photodegradation and normalized degradation of compound **1b** (2.5×10^{-5} M) in comparison with reference compound **2i** (2.5×10^{-5} M and 5×10^{-5} M, respectively) in toluene at 25.5 °C under white light irradiation.

Fatigue-resistance of bisnaphthopyran 1a–e: Fatigue is the main limitation to the commercialization of many photochromic dyes as variable-transmission materials. The presence of two photochromic units in bisnaphthopyran systems led to the investigation of these systems and their resistance against fatigue in comparison to the simple pyran systems. Fatigue-resistance of photochromic compounds has been known to be influenced by many factors.[25] On the basis of earlier work, it was far from clear whether bisphotochromic compounds would display enhanced fatigue resistance. For example, in the single report of dimeric photochromophores these are documented to be less fatigue-resistant than their monomers, presumably due to the negative influence of radical products generated from one photochromic moiety on the second unit.[5k]

The data collected in Table 2 suggest that the photochromic processes of **1a**–**e** are similar to the corresponding bithiophene substituted pyrans (compare **1a** versus **2f** and **1b** versus **2i**). These therefore provide an ideal system with which to compare the fatigue-resistance of bisnaphthopyrans. We thus performed the photodegradation measurement for **1b** in comparison with **2f** under continuous exposure to UV (366 nm) at 25 °C of a solution of **1b** or **2f**. Bisnaphthopyran **1b** provides higher colorability and better fatigue-resistance than reference **2i** at the same concentration, however, this is not the case per photochromic unit (Figure 9).

Sequential photochromism was observed for bisnaphthopyran **1a**. However, in this system both photochromic units operate, resulting in broad absorption. The open–open form is likely more susceptible to fatigue than singly open forms (closed-TC and closed-TT) as shown in Figure 10.[26]

Photochromism of quaterthiophene linked bisnaphthopyran 1f–h: The quaterthiophene-linked bisnaphthopyrans **1f**–**h** have much lower photocoloration quantum yields than the bithiophene linked bisnaphthopyrans **1a**–**e**.

In bisnaphthopyrans **1f**–**h**, there is strong absorption in the region of 300–470 nm with extinction coefficients greater than 42000 $\mathrm{M^{-1}\,cm^{-1}}$ at 406 nm in CH_2Cl_2. Under UV irradiation, strong fluorescence was observed (see Figure 11). The fluorescence quantum yield was measured to be 0.1 in **1f** relative to 9,10-diphenylanthracene,[24] which suggests that the fluorescence was derived from the quaterthiophene tether. As a result of fluorescence, the photocoloration quantum yields were small, approximately 0.1 (see Table 3). In stark contrast, the colored forms of **1a**–**h** do not have any observable fluorescence. So that even with low photocoloration quantum yield, the sequential and temperature-dependent photochromism were still observed in **1a**–**h** presumably due to lack of the pathway for intramolecular energy transfer.

Substitution effect and linking effect: In the bisnaphthopyran systems we have investigated **1a**–**h**, we have demonstrated that unusual communication between the two pyran units is possible, which results in unexpected sequential photochromism and temperature-dependent photochromism.

The absorption data for **1a**–**h** are collected in Table 4. The absorption maxima of bisnaphthopyrans were mainly determined by the electron-rich oligothiophene linkers. The absorption maximum in CH_2Cl_2 was 318 nm for molecules containing bithiophene linkers and 406 nm for those with quaterthiophene linkers, which was affected only a small amount by substitution on phenyl moiety. This also suggests

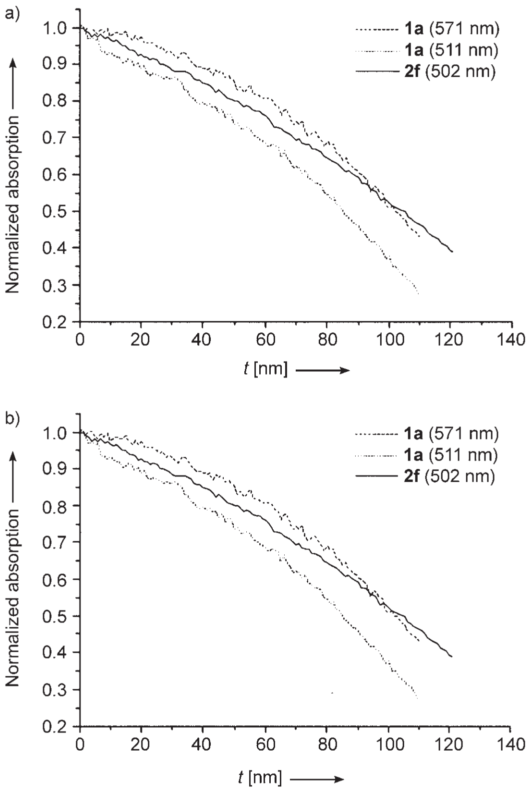


Figure 10. Photodegradation and normalized degradation of bisnaphthopyran **1a** (2.5×10^{-5} M) in comparison with reference **2f** (2.5×10^{-5} M) in toluene at 25.5 °C under white light irradiation.

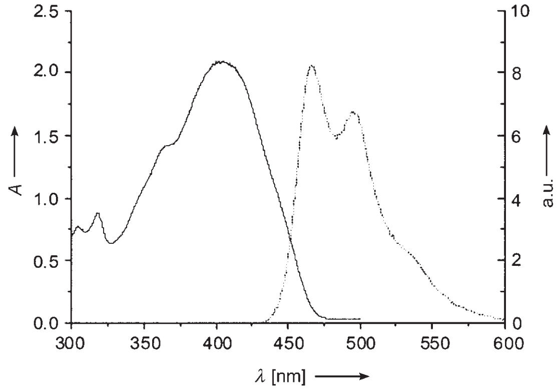


Figure 11. Absorption and fluorescence spectra of bisnaphthopyran **1f** (5.0×10^{-5} M) in chloroform at room temperature.

that the two pyran units are well insulated in bisnaphthopyrans **1a**–**h**. In contrast, the absorption maxima in the colored forms are affected both by the substitution on phenyl and by the oligothiophene linkers. In this regard, the absorption maxima of the colored forms shift bathochromically, and the colorability decreased concomitantly with the increasing electron donating ability of the *para*-substituents. Incorporation of *ortho*-substitution results in slow fading of the colored forms, as a consequence, increased colorability was observed. The slow fading allows the photochromic reaction of the second unit to take place as shown in the cases of **1a** and **1f**, wherein sequential photochromism was observed at room temperature. The value of the bathochromic shift between bisopen forms and monoopen forms are 62 nm for bithiophene linked bispyran **1a** and 25 nm for quaterthiophene linked bispyran **1f**, respectively, which suggests that interaction between the two photochromic units in bisnaphthopyrans **1f**–**h** becomes less important with the increased length of oligothiophene linker.

Table 3. Kinetic parameters of bisnaphthopyran **1f**–**h**.

Compound	Φ (300 K) toluene	Φ_f (298 K) $CHCl_3$	k [s^{-1}] (298.4 K) CH_2Cl_2
1f	0.097	0.109	0.0067
1g	–[a]	0.104	0.091
1h	–[a]	0.116	0.162

[a] Not measured.

Fatigue-resistance is normally evaluated by the time required for decrease of absorbance at absorption maximum to the half value of the initial colored forms at the photostationary state ($t_{1/2}$). However, it is difficult to maintain the measurement of fatigue-resistance under identical conditions for a long time. We thought it is more convenient in our bisnaphthopyran system to compare the relative photostability to the well-known 3,3-diphenyl-naphtho[2,1-*b*]pyran by adjusting the fatigue of 3,3-diphenyl-naphtho[2,1-*b*]pyran to about 75% in 1 h under continuous irradiation. The results are collected in Table 5.

Most of the bisnaphthopyrans display better stability than 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyran. The substitution at the *para* position of the phenyl moiety leads to better fatigue-resistance than the substitution at the *ortho* position due to increased fading rate. The photostability of bisnaphthopyran decreases with increased electron donating ability of the substituent in phenyl albeit with increased fading rate. The improved photostability of quaterthiophene linked bisnaphthopyran **1f**–**h** may be due to the low quantum yield of photochromic process.

Table 4. Absorption maxima (λ) of bisnaphthopyran **1a**–**h** (2.5×10^{-5} M) and their colored forms (λ_{col}), as well as the absorbance (A_0) of the colored forms at photostationary state under irradiation in CH_2Cl_2 at room temperature.

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
λ [nm]	318	318	318	318	318	406	406	406
λ_{col} [nm]	510 572[a]	511	515	516	520	542 567[a]	550	550
A_0	0.817 0.857[a]	0.466	0.455	0.484	0.39	1.13 1.13[a]	0.478	0.313

[a] Bisopen form (open–open).

Table 5. Relative photostability of bisnaphthopyran to 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyran in toluene at room temperature.

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
$(A_1/A_0)/$ $(A_1/A_0)_{ref}$[a]	1.04 0.88[b]	1.14	1.05	1.02	0.93	1.13 1.09[b]	1.17	1.15

[a] A_0 is absorbance of the colored forms for bispyrans at absorption maxima at photostationary state upon white light exposure, and A_1 is the absorbance of the colored forms at absorption maxima after 1 h white light illumination. $(A_0)_{ref}$ is the absorbance of the colored forms for the reference compound 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyran at its absorption maxima at photostationary state upon white light exposure, and $(A_1)_{ref}$ is the absorbance of the colored forms for the reference compound at its absorption maxima after 1 h white light irradiation. [b] Relative photostability at the longest absorption maximum of bisopen forms (open–open).

Conclusion

We have observed sequential and temperature-dependent photochromism in oligothiophene linked bisnaphthopyrans, and thus unusual interaction of the two chromophores. We have demonstrated that the cross-talk between the two photochromophores is dependent on the length of the oligothiophene linker. The presence of the bithiophene linker leads to high colorability and high quantum yield of coloration. By contrast, the quaterthiophene linker results in much diminished quantum yield and colorability. Furthermore, the quaterthiophene-linked bisnaphthopyran also renders a system displaying strong fluorescence. In all the bisnaphthopyrans studied, no fluorescence was detected for the colored forms at room temperature. The photochromic bisnaphthopyrans have similar fatigue-resistance to monopyran species. The observations we have made along with the in-depth mechanistic studies will open up new avenues for the design of novel photochromic compounds. Studies aimed at identifying other members of bisphotochromophores displaying unusual optical behavior are underway and will be reported as results become available.

Experimental Section

General information: All reactions were performed using oven dried glassware. 1,2-Dichloroethane and DMSO were dried over molecular sieves 3 Å. CH_2Cl_2 and THF were dried by passing through two 4×36 inch columns of anhydrous neutral A-2 alumina (8×14 mesh; Macherey und Nagel; activated under a flow of N_2 at 300 °C over night) to remove water. Bithiophene was synthesized according to literature method.[27] All chemicals were purchased from Aldrich and Fluka, and used as such. The solvents used for UV/Vis, IR and fluorescence study are all spectroscopic grade. 3,3-Diphenyl-[3*H*]-naphtho[2,1-*b*]pyran, 3-phenyl-3-(thiophene-2-yl)-[3*H*]-naphtho[2,1-*b*]pyran, and 3-(*p*-methoxyphenyl)-3-(thiophene-2-yl)-[3*H*]-naphtho[2,1-*b*]pyran were prepared by the reported procedure.[14]

For flash chromatography technical grade solvents were used, which were distilled prior to use. Chromatographic purification was performed as flash chromatography using Brunschwig silica 32–63, 60 Å, or MN-aluminiumoxide (neutral) with 0.3–0.5 bar pressure.

UV/Vis spectra were recorded in VARIAN Cary 50 UV/Vis spectrometer equipped with thermostated sell holder with a magnetic stirrer underneath. The data is reported as λ (ε) in the units of nm ($M^{-1}cm^{-1}$). The temperature was controlled with RM6 LAUDA thermo-cryostat. The temperature inside the cuvette was measured with a EBRO TFX 592 digital thermometer.

^1H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in $CDCl_3$, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, and integration). ^{13}C NMR spectra were recorded with ^1H decoupling on a VARIAN Mercury 75 MHz spectrometer in $CDCl_3$, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm as standard.

Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I FT-IR spectrophotometer as thin films or as solution in chloroform and are reported as cm^{-1}.

Mass spectrometric measurements were performed by the mass spectrometry service of the LOC at the ETH Zürich.

Photoreaction was generally carried out in quartz container irradiated with either 8 W or 40 W Camag UV Lamp, or with 150 W Medium Pressure Hg Lamp from Heraeus Labor UV-Reaktorsystem.

Fluorescence measurements were performed on Fluorolog-3 fluorometer (Model FL-3–22) and Aminco Bauman Series 2 Luminescence Spectrometer. To obtain accurate excitation spectra, excitation monochromator was calibrated by Xenon lamp scan. The emission monochromator was calibrated using a mercury lamp. The response of the detector was calibrated with standard tungsten/halogen lamp. Fluorescence quantum yield determination was performed in 10 mm quartz cuvette using 9,10-diphenylanthracene as the standard ($\Phi_f = 0.95$).[24] Non-degassed, spectroscopic grade chloroform was used as solvent and very dilute solutions ($A = 0.04$) were adopted in the measurements to minimize reabsorption effects.

General procedure for low-temperature chromatography: A solution of photochromic compound in a mixture of CH_2Cl_2/hexane 2:1 in a quartz container irradiated with UV (366 nm) was loaded onto a silica gel column fitted with a cooling jacket which was filled with dry ice/acetone under slight vacuum, then was eluted with initially cold CH_2Cl_2, followed by CH_2Cl_2/Et_2O 100:1 (cooled by either dry ice or liquid nitrogen) under slight vacuum. The collected fractions in thick-wall tubes were immediately frozen with liquid nitrogen.

a) Separation of closed-TC: The solution of compound **1a–c**, or **1f** in CH_2Cl_2/hexane 2:1 irradiated with UV light for 5 s at temperature ≤ −30 °C was loaded on the silica gel column, and closed-TC was separated following the general procedure.

b) Separation of closed-TT: The solution of compound **1a** or **b** in CH_2Cl_2/hexane 2:1 was irradiated with UV light for 50 s at 20 °C, the fading of color was monitored with Cary 50 at 510 nm until very slow fading was observed. This irradiation/fading procedure was repeated, then the sample was loaded on the cold silica gel column, and closed-TT was separated following the general procedure.

c) Separation of open–open: The solution of compound **1a** or **b** in CH_2Cl_2/hexane 2:1 irradiated with UV light for 4 min at temperature ≤ −30 °C was loaded on silica gel column, and open–open was separated following the general procedure.

TC and TT of compound **2f** and **i**, as well as 3,3-diphenyl-[3*H*]-naphtho-[2,1-*b*] pyran were isolated similarly by procedures to a) and b) respectively.

Low-temperature UV measurements: The frozen fraction isolated by low-temperature chromatography was transferred into a cuvette cooled to −78 °C in Oxford Cryostat while the frozen solution partially melted, then UV/Vis spectra were recorded in Cary 50 with Oxford Cryostat at −78 °C. Spectra are corrected for background absorption.

Calculation of extinction coefficient: The spectra of isolated colored forms of **1a–c**, **f**, **2f**, and **i** have the same shape as colored forms generated at room temperature by UV, however with slightly shifted absorption maxima (< 5 nm). The absorbance was recorded at −78 °C (the spectra recorded at room temperature was 85 % intensity of the one recorded at −78 °C due to the change of the volume of the solvent). The colored forms isolated were then warmed up to room temperature, and was kept in dark till complete fading of the color (if some residue color of TT or closed-TT remains, it could be bleached by irradiation with visible light). The regenerated absorption spectrum of bisnaphthopyran **1a–c**, **f**, **2f**, and **i** was compared with standard solution of **1a–c**, **f**, **2f**, and **i** so that the concentration of the colored from isolated could be obtained and the extinction coefficient of the isolated colored form (converted to the value at room temperature) could be calculated according to Lambert–Beer law.

Photocoloration and quantum yield measurements: Photocoloration kinetic measurements were carried out in thermostated cuvette irradiated with UV (366 nm) from 150 W medium pressure Hg lamp filtered through the combination of yϕc6 and C3C23 optical filters and was focused with quartz lenses using 5.0×10^{-5} M solution of photochromic compound in CH_2Cl_2. Irradiation beam of UV is at 90° angle to the monitoring beam and the absorbance was monitored at the absorption maximum of the colored form with Cary 50 UV/Vis spectrometer. The light intensity was measured with potassium ferrioxalate actinometer following standard procedure.[22]

Thermofading kinetic measurements: 5.0×10^{-5} M solution of photochromic compound in CH_2Cl_2 in thermostated cuvette was irradiated for 5 s with UV (366 nm). Once the light source was removed, the absorbance at the absorption maximum of the colored form was monitored with Cary 50. The temperature was controlled with thermocryostat to be 287.4 K.

Fatigue-resistance measurements: A stirred solution of photochromic compound in toluene was equilibrated in a thermostated cuvette for 0.5 h prior to photoirradiation. It was irradiated for 4 min with white light from 150 W Xenon lamp which was passed through a water circulated heat trap and C3C26 optical filter to eliminate heat, infrared light, and UV light less than 300 nm, then the absorbance was started to be monitored with Cary 50. The output of the white light was measured with EPM-1000 power meter.

General procedure for preparation of thienyl ketone: Tin tetrachloride (20.84 g, 80 mmol) was added dropwise under nitrogen with stirring to ice-cooled solution of thiophene (6.5 g, 77 mmol) and (substituted) benzoyl chloride (80 mmol) in CH_2Cl_2 (90 mL) over 20 min. After addition, the reaction mixture was stirred for further 10 min, then stirred at room temperature for 2.5–5 h before pouring onto mixture of crushed ice (200 g) and 5 M HCl (10 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (15 mL). The combined organic solutions were concentrated to remove most of the solvent. The residue was filtered through a plug of silica gel and washed with CH_2Cl_2. After removal of solvent, the residue was recrystallized from CH_2Cl_2/hexane. Solid was collected by filtration. The mother liquid was decolored with charcoal and recrystallized from CH_2Cl_2/hexane.

***o*-Fluorophenyl thiophene-2-yl ketone (4a)**: The general procedure was followed and the reaction was performed at 23 °C for 4 h. Brown oil was obtained in yield of 98.0 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (dd, J=5.0, 1.2 Hz, 1H), 7.62–7.48 (m, 3H), 7.27 (td, J=7.4, 1.3 Hz, 1H), 7.23–7.15 (m, 1H), 7.14 ppm (dd, J=5.0, 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=184.8, 159.4 (^{1}J=252.1 Hz), 143.9, 135.3 (^{5}J=2.4 Hz), 135.1, 132.7 (^{3}J=7.9 Hz), 130.0 (^{3}J=3.1 Hz), 127.0 (^{2}J=15.3 Hz), 124.0 (^{4}J=3.1 Hz), 116.3 ppm (^{2}J=22.0 Hz); IR ($CHCl_3$): $\tilde{\nu}$=3020, 1644, 1613, 1516, 1486, 1452, 1412, 1356, 1305, 1286, 1228, 1053, 889, 854, 769, 753 cm^{-1}.

***p*-Fluorophenyl thiophene-2-yl ketone (4b)**: The general procedure was followed and the reaction was performed at 23 °C for 2.5 h. Pale-pink solid was obtained in yield of 91.1 %. M.p. 96.8–97.5 °C (lit.[28] 98–99 °C); ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.97–7.84 (m, 2H), 7.73 (dd, J=5.0, 1.3 Hz, 1H), 7.63 (dd, J=3.7, 0.8 Hz, 1H), 7.25–7.10 (m, 3H), 2.99 (s, 1H), 2.90 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=186.7, 162.5 (^{1}J=253.8 Hz), 143.3, 134.6, 134.3, 134.3, 131.7 (^{3}J=9.6 Hz), 128.0, 115.6 ppm (^{2}J=21.3 Hz); IR ($CHCl_3$): $\tilde{\nu}$=3025, 3018, 1638, 1600, 1505, 1416, 1354, 1300, 1287, 1241, 1232, 1157, 1053, 858, 758 cm^{-1}.

Phenyl thiophene-2-yl ketone (4c): The general procedure was followed and the reaction was performed at 23 °C for 4 h. White solid was obtained in yield of 89.6 %. M.p. 52.0–52.6 °C (lit.[29] 48–50 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.90–7.82 (m, 4H), 7.73 (dd, J=5.0, 1.2 Hz, 1H), 7.65 (dd, J=3.7, 1.2 Hz, 1H), 7.63–7.55 (m, 1H), 7.54–7.46 (m, 2H), 7.17 ppm (dd, J=5.0, 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=187.9, 143.5, 138.0, 134.7, 134.0, 132.1, 129.0, 128.3, 127.8 ppm; IR ($CHCl_3$): $\tilde{\nu}$= 3023, 3013, 1637, 1600, 1515, 1448, 1414, 1354, 1290, 1232, 1053, 844, 758, 721 cm^{-1};

***p*-Methylphenyl thiophene-2-yl ketone (4d)**: The general procedure was followed and the reaction was performed at 23 °C for 3 h. Pale-pink solid was obtained in yield of 92.6 %. M.p. 75.0–75.6 °C (lit.[30] 76 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.82–7.76 (m, 2H), 7.70(dd, J=5.0, 1.3 Hz, 1H), 7.65 (d, J=3.7, 1.3 Hz, 1H), 7.33–7.27 (m, 2H), 7.16 (dd, J=5.0, 3.7 Hz, 1H), 2.45 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=187.9, 143.8, 143.0, 135.4, 134.4, 133.8, 129.3, 129.0, 127.8, 21.6 ppm; IR ($CHCl_3$): $\tilde{\nu}$= 3023, 3013, 1631, 1606, 1514, 1415, 1354, 1312, 1297, 850, 722 cm^{-1}.

***p*-Methoxyphenyl thiophene-2-yl ketone (4e)**: The general procedure was followed and the reaction was performed at 23 °C for 5 h. Colorless crystals were obtained in yield of 98.0 %. M.p. 74–75 °C (lit.[31] 73.5–74 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.94–7.87 (m, 4H), 7.69 (dd, J=5.0, 1.2 Hz, 1H), 7.65 (dd, J=3.7, 1.2 Hz, 1H), 7.16 (dd, J=5.0, 3.7 Hz, 1H), 7.02–6.92 (m, 4H), 3.90 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 186.6, 162.9, 143.7, 133.9, 133.3, 131.5, 130.6, 127.6, 113.6, 55.5 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3019, 2868, 2842, 1630, 1600, 1509, 1414, 1354, 1311, 1292, 1259, 1210, 1175, 1031, 856, 849, 758 cm^{-1}.

General procedure for preparation of 2,2′-bithiophene-5-yl ketone: Tin tetrachloride (12 mmol) was added dropwise under nitrogen with stirring to a solution of bithiophene (12 mmol) and (substituted) benzoyl chloride (16 mmol) in CH_2Cl_2 (90 mL) below 4 °C. After addition, the reaction mixture was stirred at room temperature, poured onto mixture of crushed ice (100 g) and 5 M HCl (5 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (15 mL). The combined organic solution was passed through a short silica gel column (CH_2Cl_2/ethyl acetate 10:1). Solvent was removed, the residue was recrystallized from CH_2Cl_2/hexane.

2,2′-Bithiophene-5-yl *o*-fluorophenyl ketone (4f): The general procedure was followed and the reaction was performed at 4 °C for 40 min followed by 23 °C for 1 h. Yellow-green crystals were obtained in yield of 44.5 %. M.p. 81.4–82.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.63–7.47 (m, 2H), 7.43 (dd, J=4.1, 1.9 Hz, 1H), 7.40–7.31 (m, 2H), 7.30–7.12 (m, 3H), 7.08 ppm (dd, J=5.3, 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=184.6, 159.7 (^{1}J=252.7 Hz), 147.3, 141.9, 136.4, 136.3, 132.9 (^{3}J=8.6 Hz), 130.3 (^{3}J=3.4 Hz), 128.4, 126.9, 126.0, 124.3, 124.3 (^{4}J=4.9 Hz), 116.5 ppm (^{2}J=22.0 Hz); IR ($CHCl_3$): $\tilde{\nu}$=3078, 3020, 3013, 1637, 1613, 1508, 1485, 1445, 1422, 1314, 1315, 1228, 1058, 875, 815, 757, 703 cm^{-1}.

2,2′-Bithiophene-5-yl naphthalene-2-yl ketone (4g): The general procedure was followed and the reaction was performed 23 °C for 2 h. Yellow solid was obtained in yield of 62.0 %. M.p. 139.3–139.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.40 (s, 1H), 8.02–7.88 (m, 4H), 7.63 (d, J= 4.0 Hz, 1H), 7.66–7.54 (m, 2H), 7.38 (dd, J=3.7, 1.2 Hz, 1H), 7.36 (dd, J=5.3, 1.2 Hz, 1H), 7.25 (d, J=3.7 Hz, 1H), 7.09 ppm (dd, J=5.3, 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=187.4, 146.0, 141.6, 136.2, 135.7, 135.1, 135.0, 132.2, 130.1, 129.1, 128.3, 128.2, 128.0, 127.7, 126.7, 126.5, 125.7, 125.1, 124.0 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3063, 3026, 3012, 1625, 1507, 1466, 1447, 1422, 1354, 1311, 1297, 1236, 1226, 1058, 810, 794, 722, 702 cm^{-1}.

2,2′-Bithiophene-5-yl *p*-Methoxyphenyl ketone (4h): The general procedure was followed and the reaction was performed at 23 °C for 20 min. Yellow-green crystals were obtained in yield of 67.7 %. M.p. 119.0–119.6 °C (lit.[16] 119–120 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.94–7.86 (m, 4H), 7.55 (d, J=4.0 Hz, 1H), 7.35 (dd, J=3.7, 0.9 Hz, 1H), 7.33 (dd, J=5.3, 1.2 Hz, 1H), 7.21 (d, J=3.7 Hz, 1H), 6.97 (dd, J=5.3, 3.7 Hz, 1H), 7.03–6.96 (m, 4H), 3.90 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=186.2, 162.8, 145.3, 141.7, 136.3, 134.8, 131.3, 130.4, 128.1, 126.3, 125.5, 123.9, 113.6, 95.6, 55.5 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3076, 3013, 2967, 2842, 1624, 1600, 1573, 1506, 1447, 1423, 1315, 1293, 1259, 1214, 1175, 1058, 1131, 869, 844, 810, 701 cm^{-1}.

2,2′-Bithiophene-5-yl *p*-fluorophenyl ketone (4i): The general procedure was followed and the reaction was performed at 23 °C for 70 min. Yellow solid was obtained in yield of 57.8 %. M.p. 115.3–115.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.96–7.82 (m, 2H), 7.53 (d, J=3.4 Hz, 1H), 7.40–

7.30 (m, 2H), 7.24–7.11 (m, 3H), 7.08 ppm (dd, J=5.0, 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=186.4, 165.4 (^{1}J=253.9 Hz), 146.5, 141.4, 136.3, 134.4, 131.7, 131.6 (^{3}J=8.5 Hz), 128.4, 126.8, 125.9, 124.2, 115.7 ppm (^{2}J=22.0 Hz).

1-Phenyl-1-(thiophene-2-yl)-prop-2-yn-1-ol (5c): Lithium acetylide diamine complex (15 mmol) in dry DMSO (25 mL) was added to *p*-aromatic ketone (15 mmol) in portions with stirring over 20 min. After addition, the reaction mixture was stirred at room temperature for 2 h, poured onto crushed ice, CH_2Cl_2 (30 mL) was added, filtered through Celite, extracted with CH_2Cl_2. The mixture was dried over anhydrous sodium sulfate, filtered, and purified by flush chromatography (silica gel, hexane/CH_2Cl_2 1:2). Evaporation of the solvent gave yellow oil in yield of 76.8%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.73–7.68 (m, 2H), 7.42–7.29 (m, 3H), 7.27 (dd, J=5.0, 1.2 Hz, 1H), 7.09 (dd, J=3.7, 1.2 Hz, 1H), 6.92 (dd, J=5.0, 3.7 Hz, 1H), 3.02 (s, 1H), 2.99 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=149.3, 143.5, 128.2, 128.1, 126.3, 126.0, 125.6, 125.5, 85.7, 74.9, 71.7 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3582, 3306, 3068, 3029, 3013, 2119, 1601, 1491, 1450, 1434, 1353, 1324, 1234, 1180, 1160, 1031, 973, 958, 834, 701 cm^{-1}.

General procedure for preparation of propargyl alcohol: Sodium acetylide (1.4–2.2 equiv) suspended in dry DMSO (25 mL) was added aromatic ketone (25 mmol) in portions with stirring over 20 min under water bath cooling while bubbling acetylene gas. After addition, the reaction mixture was stirred at room temperature for 2 h, poured onto crushed ice, acidified with 4 M HCl until the pH was approximately 6. After extraction with CH_2Cl_2 (20 mL, then 2×10 mL), the mixture was dried over anhydrous sodium sulfate and filtered. Evaporation of the solvent, the resulted oil was purified by flush chromatography on neutral alumina (activity III) (hexane/CH_2Cl_2 2:1).

1-(*o*-Fluorophenyl)-1-(thiophene-2-yl)-prop-2-yn-1-ol (5a): The general procedure was followed using 1.5 equiv of sodium acetylide as base and yellow-brown oil was obtained in yield of 60.2%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.70 (td, J=8.1, 1.9 Hz, 1H), 7.40–7.30 (m, 1H), 7.30 (dd, J=5.4, 1.3 Hz, 1H), 7.17 (td, J=7.8, 1.3 Hz, 1H), 7.14 (ddd, J=3.7, 1.3, 0.6 Hz, 1H), 7.04 (dd, J=11.5, 8.1, 1.3 Hz, 1H), 6.95 (dd, J=5.0, 3.4 Hz, 1H), 3.26 (d, J=3.4 Hz, 1H), 2.87 ppm (d, J=0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.8 (^{1}J=248.4 Hz), 147.6, 130.6 (^{2}J=9.4 Hz), 130.2 (^{3}J=8.5 Hz), 127.0 (^{3}J=1.8 Hz), 126.4, 126.1, 125.7, 123.8 (^{4}J=3.0 Hz), 116.2 (^{1}J=21.4 Hz), 84.1, 74.5 (^{5}J=2.2 Hz), 69.0 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3586, 3306, 3080, 3068, 3030, 3013, 2123, 1614, 1586, 1488, 1453, 1354, 1332, 1273, 1230, 1179, 1151, 1026, 973, 839, 706 cm^{-1}.

1-(*p*-Fluorophenyl)-1-(thiophene-2-yl)-prop-2-yn-1-ol (5b): The general procedure was followed using 1.5 equiv of sodium acetylide as base and yellow-brown oil was obtained in yield of 82.4%. ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.73–7.61 (m, 2H), 7.28 (dd, J=5.0, 1.3 Hz, 1H), 7.09 (dd, J=3.7, 1.3 Hz, 1H), 7.10–6.98 (m, 2H), 6.93 (dd, J=5.0, 3.7 Hz, 1H), 2.99 (s, 1H), 2.90 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=162.7 (^{1}J=246.6 Hz), 149.5, 139.6 (^{4}J=2.6 Hz), 127.7 (^{3}J=7.6 Hz), 126.6, 126.4, 125.7, 115.2 (^{2}J=22.0 Hz), 85.5, 75.1, 71.2 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3582, 3305, 3078, 3020, 2120, 1604, 1508, 1410, 1354, 1322, 1234, 1209, 1160, 1035, 975, 959, 837, 706 cm^{-1}.

1-(*p*-Methylphenyl)-1-(thiophene-2-yl)-prop-2-yn-1-ol (5d): The general procedure was followed using 1.5 equiv of sodium acetylide as base and yellow-brown oil was obtained in yield of 86.6%. ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.62–7.53 (m, 2H), 7.26(dd, J=5.0, 1.2 Hz, 1H), 7.23–7.13 (m, 2H), 7.10 (dd, J=3.7, 1.2 Hz, 1H), 6.92 (dd, J=5.0, 3.7 Hz, 1H), 2.96 (s, 1H), 2.88 (s, 1H), 2.36 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=149.8, 141.0, 138.2, 129.0, 126.5, 126.1, 125.7, 125.6, 85.8, 74.8, 71.6, 21.0 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3582, 3306, 3068, 3020, 3012, 2925, 2868, 2119, 1611, 1511, 1434, 1353, 1323, 1234, 1182, 1035, 972, 960, 845, 837, 812, 706 cm^{-1}.

1-(*p*-Methoxyphenyl)-1-(thiophene-2-yl)-prop-2-yn-1-ol (5e): The general procedure was followed using 2.0 equiv of sodium acetylide as base and brown oil was obtained in yield of 84.1%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.64–7.57 (m, 2H), 7.26 (dd, J=5.0, 1.2 Hz, 1H), 7.08 (dd, J=3.7, 1.2 Hz, 1H), 6.92 (dd, J=5.0, 3.7 Hz, 1H), 6.91–6.85 (m, 2H), 3.81 (s, 3H), 2.93 (s, 1H), 2.88 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.2, 149.6, 135.8, 127.0, 126.3, 125.9, 125.3, 113.4, 85.8, 74.8, 71.4, 55.3 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3582, 3306, 3020, 2960, 2840, 2119, 1608, 1585, 1510, 1464, 1304, 1252, 1176, 1036, 972, 959, 832, 706 cm^{-1}.

1-(2,2′-Bithiophene-5-yl)-1-(*o*-fluorophenyl)prop-2-yn-1-ol (5f): The general procedure was followed using 2.2 equiv of sodium acetylide as base and yellow-brown oil was obtained in yield of 82.7%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.75 (td, J=8.1, 1.9 Hz, 1H), 7.41–7.31 (m, 1H), 7.24–7.16(m, 2H), 7.13 (dd, J=3.4, 1.2 Hz, 1H), 7.10 (ddd, J=11.6, 3.4, 1.2 Hz, 1H), 7.05 (d, J=3.7 Hz, 1H), 7.00 (d, J=3.7 Hz, 1H), 6.99 (dd, J=5.0, 3.4 Hz, 1H), 3.31 (s, 1H), 3.30 (s, 1H), 2.90 (s, 1H), 2.89 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=160.0 (^{1}J=248.1 Hz), 146.4, 138.2, 137.0, 130.4 (^{3}J=8.6 Hz), 130.4 (^{2}J=6.3 Hz), 127.8, 127.1 (^{2}J=1.5 Hz), 126.3, 124.6, 124.0 (^{4}J=3.7 Hz), 124.0, 122.9, 116.3 (^{2}J=20.6 Hz), 83.8, 69.0 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3025, 3018, 1638, 1600, 1505, 1416, 1354, 1300, 1287, 1241, 1232, 1157, 1053, 858, 758 cm^{-1}.

1-(2,2′-Bithiophene-5-yl)-1-(naphthalene-2-yl)prop-2-yn-1-ol (5g): The general procedure was followed using 2.0 equiv of sodium acetylide as base and yellow-brown oil was obtained in yield of 86.6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.25 (d, J=1.9 Hz, 1H), 7.96–7.80 (m, 3H), 7.74 (dd, J=8.7, 1.9 Hz, 1H), 7.58–7.46 (m, 2H), 7.19 (dd, J=5.3, 1.2 Hz, 1H), 7.11 (dd, J=3.7, 1.2 Hz, 1H), 7.04 (d, J=3.7 Hz, 1H), 7.01–6.92 (m, 2H), 3.08 (s 1H), 2.97 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.8, 140.3, 138.2, 136.8, 132.9, 132.9, 128.4, 128.2, 127.6, 127.5, 126.4, 126.2, 124.5, 124.0, 123.9, 123.7, 122.8, 85.2, 75.4, 71.7 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3580, 3305, 3062, 3012, 2958, 2929, 2118, 1601, 1508, 1466, 1425, 1356, 1315, 1270, 1228, 1119, 1037, 979, 942, 894, 858, 820, 798, 698 cm^{-1}.

1-(2,2′-Bithiophene-5-yl)-1-(*p*-methoxyphenyl)prop-2-yn-1-ol (5h): The general procedure was followed using 1.68 equiv of sodium acetylide as base and yellow-brown oil was obtained in yield of 71.0%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.67–7.60 (m, 2H), 7.19 (dd, J=5.0, 1.2 Hz, 1H), 7.12 (dd, J=3.7, 1.2 Hz, 1H), 7.01–6.95 (m, 3H), 7.94–7.87 (m, 2H), 3.82 (s, 3H), 3.03 (s, 1H), 2.90 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.4, 148.3, 137.9, 137.0, 135.4, 127.6, 127.0, 125.9, 124.5, 123.7, 113.5, 85.5, 75.0, 71.4, 55.3 ppm; IR ($CHCl_3$): $\tilde{\nu}$=3581, 3305, 3076, 3020, 3012, 2960, 2840, 2118, 1608, 1585, 1510, 1465, 1304, 1253, 1176, 1036, 973, 957, 829, 805, 698 cm^{-1}.

1-(2,2′-Bithiophene-5-yl)-1-(*p*-fluorophenyl)prop-2-yn-1-ol (5i): The general procedure was followed using 2.2 equiv of sodium acetylide as base and yellow-brown oil was obtained in yield of 82.7%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.74–7.65 (m, 2H), 7.21 (dd, J=5.0, 1.2 Hz, 1H), 7.12 (dd, J=3.7, 1.2 Hz, 1H), 7.11–7.02 (m, 2H), 7.02–6.96 (m, 3H), 3.04 (s, 1H), 2.92 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=162.5 (^{1}J=247.8 Hz), 147.9, 139.2, 138.4, 127.8, 127.6 (^{3}J=8.5 Hz), 126.2, 124.7, 123.9, 122.9, 115.2 (^{2}J=22.0 Hz), 85.1, 75.3, 71.2 ppm.

General procedure for preparation of naphthopyran 2: Propargyl alcohol **5** (1.05 mmol) and 2-naphthol (144.2 mg, 1 mmol) in the presence of PPTS (12.6 mg, 0.05 mmol) and trimethyl orthoformate (0.21 mL, 2 mmol) in 1,2-dichloroethane (2 mL) was refluxed for 2 h or stirred at 23 °C for 3–4.5 h followed by 0.5–1 h reflux. Solvent was removed in vacuo and the residue was purified by chromatography (silica gel, CH_2Cl_2/hexane 2:1), and recrystallization from CH_2Cl_2/hexane (or dried under high vacuum).

3-(*o*-Fluorophenyl-3-(thiophene-2-yl)-[3*H*]-naphtho[2,1-*b*]pyran (2a): The general procedure was followed and the reaction was performed under reflux for 2 h, pale-yellow solid was obtained in yield of 88.8%. M.p. 118–118.5 °C (lit.[11] 116 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.97 (d, J=8.3 Hz, 1H), 7.76 (td, J=8.1, 1.9 Hz, 1H), 7.74 (d, J=8.1 Hz, 1H), 7.70 (d, J=9.0 Hz, 1H), 7.49 (ddd, J=8.4, 6.9, 1.6 Hz, 1H), 7.35 (ddd, J=8.1, 6.9, 1.2 Hz, 1H), 7.33–7.20 (m, 4H), 7.14 (td, J=7.5, 1.2 Hz, 1H), 7.04 (ddd, J=11.5, 8.1, 1.2 Hz, 1H), 7.01–6.96 (m, 1H), 6.92 (dd, J=5.0, 3.4 Hz, 1H), 6.50 ppm (dd, J=10.0, 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.5 (^{1}J=249.0 Hz), 150.1, 148.1, 131.2 (^{2}J=11.0 Hz), 130.0 (^{3}J=11.0 Hz), 129.8, 129.6, 128.6, 127.6 (^{3}J=3.7 Hz), 126.8, 126.5, 126.4, 126.2, 125.8 (^{5}J=3.7 Hz), 123.9, 123.9 (^{4}J=3.7 Hz), 121.4, 119.8, 118.2, 116.5 (^{2}J=23.2 Hz), 113.8, 78.2 ppm (^{3}J=2.6 Hz); UV (toluene): λ_{max} (ε) = 306sh (20700), 317 (23400 mol^{-1} dm^{3} cm^{-1}); IR (KBr): $\tilde{\nu}$=3062, 1632, 1602, 1584, 1504, 1460, 1224, 1205, 1177, 1159, 1086, 1003, 952, 825, 814, 749, 725, 696 cm^{-1}; HRMS (MALDI): *m*/*z* (%): calcd for $C_{23}H_{15}FOS$: 359.0911; found: 359.0914 (100) [M+H^{+}].

3-(*p*-Fluorophenyl-3-(thiophene-2-yl)-[3*H*]-naphtho[2,1-*b*]pyran (2b): The general procedure was followed and the reaction was performed under reflux for 2 h, colorless solid was obtained in yield of 98.2%. M.p. 122.5–124°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.97 (d, J=8.4 Hz, 1H), 7.73 (d, J=8.1 Hz, 1H), 7.68 (d, J=9.0 Hz, 1H), 7.60–7.51 (m, 2H), 7.49 (ddd, J=8.4, 7.2, 1.2 Hz, 1H), 7.34 (ddd, J=8.1, 6.8, 1.2 Hz, 1H), 7.32 (d, J=9.7 Hz, 1H), 7.29 (dd, J=5.0, 1.6 Hz, 1H), 7.19 (d, J=8.7 Hz, 1H), 7.08–6.88 (m, 4H), 6.25 ppm (d, J=10.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ=162.4 (^1J=246.6 Hz), 150.3, 149.3, 140.4, 130.2, 129.8, 129.6, 128.7, 128.4 (^3J=7.3 Hz), 127.1, 126.9, 126.5, 123.9, 121.3, 120.0, 118.3, 115.0 (^2J=20.8 Hz), 113.9, 80.0 ppm; IR (KBr): $\tilde{\nu}$=3062, 1632, 1602, 1585, 1504, 1461, 1224, 1206, 1177, 1159, 1086, 1003, 952, 825, 814, 749, 726, 696 cm^{-1}; HRMS (MALDI): m/z (%): calcd for C$_{23}$H$_{15}$FOS: 359.0911; found: 359.0913 (100) [M+H$^+$].

3-(*p*-Methylphenyl)-3-(thiophene-2-yl)-[3*H*]-naphtho[2,1-*b*]pyran (2d): The general procedure was followed and the reaction was performed under reflux for 2 h, white solid was obtained in yield of 95.3%. M.p. 159.2–159.6°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.96 (d, J=8.4 Hz, 1H), 7.72 (dd, J=8.1, 0.6 Hz, 1H), 7.67 (d, J=8.7 Hz, 1H), 7.51–7.43 (m, 3H), 7.32 (ddd, J=8.1, 6.8, 0.9 Hz, 1H), 7.32–7.26 (m, 2H), 7.20 (d, J=8.7 Hz, 1H), 7.18–7.10 (m, 2H), 6.95 (dd, J=3.4, 1.2 Hz, 1H), 6.91 (dd, J=5.0, 3.4 Hz, 1H), 6.28 (d, J=10.0 Hz, 1H), 2.33 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ=150.3, 149.5, 141.5, 137.5, 129.9, 129.7, 129.4, 128.7, 128.5, 126.1, 127.4, 126.6, 126.3, 123.6, 121.3, 119.6, 118.3, 113.8, 80.2, 21.1 ppm; IR (KBr): $\tilde{\nu}$=3084, 3022, 2918, 1634, 1510, 1461, 1435, 1244, 1236, 1104, 1091, 1005, 808, 751, 711 cm^{-1}; HRMS (MALDI): m/z (%): calcd for C$_{24}$H$_{18}$OS: 355.1162; found: 355.1164 (100) [M+H$^+$].

3-(2,2′-Bithiophene-5-yl)-3-(*o*-fluorophenyl)-[3*H*]-naphtho[2,1-*b*]pyran (2f): The general procedure was followed and the reaction was performed at 23°C for 4 h followed by 1 h reflux, pale-purple foam was obtained in yield of 89.2%. ^{1}H NMR (300 MHz, CDCl$_3$): δ=8.00 (d, J=8.1 Hz, 1H), 7.83 (td, J=8.1, 1.9 Hz, 1H), 7.76 (d, J=8.1 Hz, 1H), 7.73 (d, J=9.0 Hz, 1H), 7.50 (ddd, J=8.1, 6.9, 1.2 Hz, 1H), 7.41–7.26 (m, 4H), 7.18 (dd, J=5.0, 1.2 Hz, 1H), 7.17 (td, J=7.4, 1.2 Hz, 1H), 7.11 (dd, J=3.7, 1.2 Hz, 1H), 7.08 (ddd, J=11.5, 8.1, 1.2 Hz, 1H), 6.99 (d, J=3.7 Hz, 1H), 6.97 (dd, J=5.3, 3.7 Hz, 1H), 6.91 (d, J=3.7 Hz, 1H), 6.52 ppm (dd, J=10.0, 4.7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ=159.5 (^1J=250.3 Hz), 150.0, 146.8, 138.5, 137.3, 130.9 (^2J=11.0 Hz), 130.2, 130.0 (^3J=8.7 Hz), 129.8, 129.7, 128.6, 127.8, 127.6 (^3J=2.4 Hz), 126.9, 126.8, 125.3 (^5J=4.9 Hz), 124.6, 124.0, 123.9 (^4J=3.5 Hz), 123.1, 121.4, 120.1, 118.2, 116.5 (^1J=22.0 Hz), 113.8, 78.2 ppm (^3J=2.3 Hz); IR (KBr): $\tilde{\nu}$=3065, 1634, 1582, 1515, 1483, 1460, 1449, 1272, 1230, 1204, 1082, 1002, 803, 759, 747, 694 cm^{-1}; UV (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) = 306sh (20700), 317 (23300 mol^{-1}dm^{3}cm^{-1}); UV (toluene): $\lambda_{\max}$ (ε) = 306sh (20000), 317 (22800 mol^{-1}dm^{3}cm^{-1}); HRMS (MALDI): m/z (%): calcd for C$_{27}$H$_{17}$FOS$_2$: 441.0778; found: 441.0774 (100) [M+H$^+$].

3-(2,2′-Bithiophene-5-yl)-3-(naphthalene-2-yl)-[3*H*]-naphtho[2,1-*b*]pyran (2g): The general procedure was followed and the reaction was performed at 23°C for 3.5 h followed by 1 h reflux, yellow orange solid was obtained in yield of 92.4%. M.p. 189–190°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ=8.09 (d, J=1.8 Hz, 1H), 7.99 (d, J=8.4 Hz, 1H), 7.88–7.78 (m, 3H), 7.77–7.67 (m, 3H), 7.54–7.43 (m, 3H), 7.39 (d, J=9.7 Hz, 1H), 7.33 (ddd, J=8.1, 6.8, 1.2 Hz, 1H), 7.28 (d, J=8.3 Hz, 1H), 7.17 (dd, J=5.0, 1.2 Hz, 1H), 7.09 (dd, J=3.7, 1.2 Hz, 1H), 6.97 (d, J=4.7 Hz, 1H), 6.96 (dd, J=5.0, 3.7 Hz, 1H), 6.89 (d, J=3.7 Hz, 1H), 6.36 ppm (d, J=9.7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ=150.4, 148.1, 141.3, 137.3, 133.0, 132.9, 130.3, 129.9, 129.6, 128.7, 128.6, 128.2, 127.8, 127.7, 127.4, 126.4, 126.3, 125.4, 124.6, 123.9, 123.0, 121.4, 120.4, 118.4, 114.0, 80.5 ppm; IR (KBr): $\tilde{\nu}$=3101, 3053, 1629, 1586, 1512, 1461, 1426, 1240, 1203, 1182, 1085, 1035, 1010, 828, 806, 747, 693 cm^{-1}; HRMS (MALDI): m/z (%): calcd for C$_{31}$H$_{20}$OS$_2$: 473.1028; found: 473.1028 (100) [M^+].

3-(2,2′-Bithiophene-5-yl)-3-(*p*-methoxyphenyl)-[3*H*]-naphtho[2,1-*b*]pyran (2h): The general procedure was followed and the reaction was performed at 23°C for 3.5 h followed by 0.5 h reflux, light purple foam was obtained in yield of 83.5%. ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.98 (d, J=8.1 Hz, 1H), 7.73 (d, J=8.1 Hz, 1H), 7.68 (d, J=9.0 Hz, 1H), 7.57–7.50 (m, 2H), 7.48 (ddd, J=8.4, 6.8, 1.6 Hz, 1H), 7.34 (ddd, H=8.1, 6.8, 0.9 Hz, 1H), 7.32 (d, J=9.7 Hz, 1H), 7.20 (d, J=9.0 Hz, 1H), 7.17 (dd, J=5.0, 1.2 Hz, 1H), 7.09 (dd, J=3.7, 1.2 Hz, 1H), 6.97 (d, J=3.7 Hz, 1H), 6.96 (dd, J=5.0, 3.7 Hz, 1H), 6.92–6.85 (m, 2H), 6.84 (d, J=3.7 Hz, 1H), 6.25 (d, J=9.7 Hz, 1H), 3.79 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ=159.4, 150.4, 148.6, 138.3, 137.4, 136.3, 130.1, 129.9, 129.6, 128.6, 127.8, 127.1, 127.0, 126.8, 124.5, 123.8, 122.9, 121.4, 119.9, 118.4, 113.9, 113.5, 80.2, 55.2 ppm; IR (KBr): $\tilde{\nu}$=3060, 2952, 2930, 2833, 1633, 1607, 1584, 1509, 1460, 1438, 1251, 1203, 1175, 1083, 1034, 999, 806, 746, 695 cm^{-1}; HRMS (MALDI): m/z (%): calcd for C$_{28}$H$_{20}$O$_2$S$_2$: 453.0977; found: 453.0976 (100) [M+H$^+$].

3-(2,2′-Bithiophene-5-yl)-3-(*p*-fluorophenyl)-[3*H*]-naphtho[2,1-*b*]pyran (2i): The general procedure was followed and the reaction was performed at 23°C for 4.5 h followed by 1 h reflux, beige solid was obtained in yield of 94.5%. M.p. 155.5–156.3°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.98 (d, J=8.7 Hz, 1H), 7.74 (d, J=8.1 Hz, 1H), 7.69 (d, J=8.7 Hz, 1H), 7.63–7.54 (m, 2H), 7.50 (ddd, J=8.4, 6.9, 1.2 Hz, 1H), 7.35 (ddd, J=8.1, 6.8, 0.9 Hz, 1H), 7.34 (d, J=10.0 Hz, 1H), 7.20 (d, J=10.0 Hz, 1H), 7.17 (dd, J=5.3, 0.9 Hz, 1H), 7.10 (dd, J=3.4, 0.9 Hz, 1H), 7.09–6.99 (m, 2H), 6.97 (dd, J=5.0, 3.7 Hz, 1H), 6.96 (d, J=3.7 Hz, 1H), 6.84 (d, J=4.0 Hz, 1H), 6.23 ppm (d, J=10.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ=162.5 (^1J=246.6 Hz), 150.2, 148.0, 140.0, 138.6, 137.2, 130.3, 129.9, 129.7, 128.7, 128.4 (^3J=8.5 Hz), 127.8, 127.2, 126.9, 126.7, 124.7, 123.9, 122.9, 121.4, 120.3, 118.3, 115.1 (^2J=22.0 Hz), 113.9, 80.0 ppm; IR (KBr): $\tilde{\nu}$=3070, 1632, 1603, 1584, 1503, 1459, 1231, 1209, 1157, 1084, 1046, 986, 828, 815, 796, 748, 692 cm^{-1}; UV (toluene): $\lambda_{\max}$ (ε) = 306sh (21000), 317 (23600 mol^{-1}dm^{3}cm^{-1}); HRMS (MALDI): m/z (%): calcd for C$_{27}$H$_{17}$FOS$_2$: 441.0778; found: 441.0774 (100) [M+H$^+$].

General procedure for preparation of bispyran 1: Butyl lithium (1.6 M, 0.5 mL, 0.8 mmol) was added dropwise with stirring to a solution of naphthopyran **2** (0.5 mmol) in dry THF (4 mL) at −78°C under nitrogen. The mixture was stirred for 0.5 h, anhydrous cupric chloride (1.6–2.2 equiv) was added in one portion. Stirring was continued for 2 h then slowly warm up to room temperature and stirred overnight. Crushed ice (10 g) was added to the reaction mixture. After acidification with 4 M HCl until the pH was approximately 1, the mixture was extracted with CH$_2$Cl$_2$ (25 mL, then 2×10 mL). The combined organic solution was dried over anhydrous sodium sulfate. If any solid was suspended in CH$_2$Cl$_2$, heating was applied to dissolve the solid, cooled to room temperature and then dried. Subsequently, it was filtered and passed through a short silica gel column washed with CH$_2$Cl$_2$. After removal of the most of the solvent until the total volume was approximately 5 mL, the mixture was heated to reflux, cooled down and allowed to stand at room temperature. The resulting solid was filtered and washed with a small volume of CH$_2$Cl$_2$. The solid was collected and purified by chromatography (silica gel, hexane/CH$_2$Cl$_2$ 1:1) and recrystallized from CH$_2$Cl$_2$/hexane.

5,5′-Bis[3-(*o*-fluorophenyl)-[3H]-naphtho[2,1-*b*]pyran-3-yl]-2,2′-bithiophene (1a): The general procedure was followed and 2.0 equiv of CuCl$_2$ was used, pink solid was obtained in yield of 72.7%. M.p. 206–207°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.96 (d, J=8.4 Hz, 2H), 7.76 (ddd, J=9.7, 7.8, 1.9 Hz, 1H), 7.73 (d, J=7.8 Hz, 1H), 7.69 (d, J=9.0 Hz, 1H), 7.54–7.42 (m, 1H), 7.40–7.24 (m, 3H), 7.22 (d, J=8.7 Hz, 1H), 7.18–7.09 (m, 1H), 7.08–6.96 (m, 1H), 6.88 (d, J=3.7 Hz, 1H), 6.83 (d, J=3.7 Hz, 1H), 6.44 ppm (dd, J=10.0, 4.4 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ=159.1 (^1J=247.8 Hz), 149.7, 146.6, 138.0, 130.6 (^2J=11.0 Hz), 130.0, 129.8 (^3J=7.9 Hz), 129.6, 129.4, 128.4, 127.3 (^3J=2.8 Hz), 126.7, 126.7, 125.1 (^5J=4.3 Hz), 123.8, 123.8 (^4J=3.3 Hz), 122.9, 121.2, 120.0, 118.0, 116.3 (^2J=21.9 Hz), 113.6, 78.1 ppm (^3J=2.5 Hz); IR (KBr): $\tilde{\nu}$=3065, 2956, 1635, 1613, 1581, 1512, 1482, 1446, 1238, 1207, 1082, 987, 800, 748 cm^{-1}; UV (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) = 306sh (26800), 318 (33800), 333sh (28100 mol^{-1}dm^{3}cm^{-1}); UV (toluene): $\lambda_{\max}$ (ε) = 306sh (25700), 318 (32900), 333sh (28300 mol^{-1}dm^{3}cm^{-1}); HRMS (MALDI): m/z (%): calcd for C$_{46}$H$_{28}$F$_2$O$_2$S$_2$: 714.1493; found: 714.1496 (100) [M^+].

5,5′-Bis[3-(*p*-fluorophenyl)-[3*H*]-naphtho[2,1-*b*]pyran-3-yl]-2,2′-bithiophene (1b): The general procedure was followed and 2.0 equiv of CuCl$_2$ was used, beige solid was obtained in yield of 55.0%. M.p. 200–201°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.96 (d, J=8.1 Hz, 1H), 7.73 (d, J=7.8 Hz, 1H), 7.67 (d, J=8.7 Hz, 1H), 7.59–7.50 (m, 2H), 7.48 (ddd, J=8.4, 6.9, 1.3 Hz, 1H), 7.34 (ddd, J=8.1, 7.2, 1.2 Hz, 1H), 7.32 (d, J=10.3 Hz, 1H), 7.17 (d, J=8.7 Hz, 1H), 7.07–6.96 (m, 2H), 6.88 (d, J=

3.7 Hz, 1H), 6.80 (d, $J = 3.7$ Hz, 1H), 6.18 ppm (d, $J = 10.0$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 162.5$ ($^{1}J = 247.8$ Hz), 150.2, 148.2, 140.0 ($^{4}J = 3.7$ Hz), 138.3, 130.3, 129.8, 129.6, 128.7, 128.4 ($^{3}J = 8.6$ Hz), 127.2, 126.9, 126.7, 123.9, 123.0, 121.4, 120.3, 118.3, 115.1 ($^{2}J = 22.0$ Hz), 113.8, 80.0 ppm; IR (KBr): $\tilde{\nu} = 3067$, 1632, 1608, 1588, 1508, 1461, 1240, 1202, 1158, 1085, 1004, 834, 802, 751 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max} (ε) = 306 sh (26200), 318 (33200), 333 sh (28000 mol^{-1} dm^3 cm^{-1}); UV (toluene): λ_{max} (ε) = 306 sh (26700), 318 (33800), 333 sh (28400 mol^{-1} dm^3 cm^{-1}); HRMS (MALDI): *m*/*z* (%): calcd for $C_{46}H_{28}F_2O_2S_2$: 714.1493; found: 714.1498 (100) [M^+].

5,5′-Bis[3-phenyl-3*H*]-naphtho[2,1-*b*]pyran-3-yl]-2,2′-bithiophene 1c: The general procedure was followed and 2.0 equiv of CuCl$_2$ was used, beige solid was obtained in yield of 96.5%. M.p. 244–245 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.95$ (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 9.0$ Hz, 1H), 7.60–7.53 (m, 2H), 7.51–7.43 (m, 1H), 7.40–7.24 (m, 5H), 7.18 (d, $J = 8.7$ Hz, 1H), 6.87 (d, $J = 3.7$ Hz, 1H), 6.80 (d, $J = 3.7$ Hz, 1H), 6.23 ppm (d, $J = 10.0$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 150.1$, 148.1, 143.9, 138.0, 129.9, 129.6, 129.4, 128.4, 128.0, 127.8, 127.1, 126.7, 126.6, 126.2, 123.6, 122.7, 121.2, 119.9, 118.2, 113.7, 80.3 ppm; IR (KBr): $\tilde{\nu} = 3061$, 3026, 1630, 1588, 1515, 1460, 1446, 1244, 1215, 1202, 1088, 1004, 905, 806, 754, 729, 697 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max} (ε) = 306 sh (22400), 318 (28500), 333 sh (24100 mol^{-1} dm^3 cm^{-1}); UV (toluene): λ_{max} (ε) = 306 sh (19800), 318 (25500), 333 sh (21800 mol^{-1} dm^3 cm^{-1}); HRMS (MALDI): *m*/*z* (%): calcd for $C_{46}H_{30}O_2S_2$: 679.1760; found: 679.1752 (100) [M+H$^+$].

5,5′-Bis[3-(*p*-methylphenyl)-[3*H*]-naphtho[2,1-*b*]pyran-3-yl]-2,2′-bithiophene (1d): The general procedure was followed and 2.0 equiv of CuCl$_2$ was used, beige solid was obtained in yield of 77.1%. M.p. 206–207 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.95$ (d, $J = 8.1$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.65 (d, $J = 9.0$ Hz, 1H), 7.42–7.52 (m, 3H), 7.32 (ddd, $J = 8.1$, 6.8, 0.9 Hz, 1H), 7.29 (d, $J = 9.7$ Hz, 1H), 7.18 (d, $J = 8.7$ Hz, 1H), 7.16–7.10 (m, 1H), 6.86 (d, $J = 3.7$ Hz, 1H), 6.80 (d, $J = 3.7$ Hz, 1H), 6.21 (d, $J = 10.0$ Hz, 1H), 2.32 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 150.4$, 148.6, 141.3, 138.2, 137.7, 130.1, 129.9, 129.6, 128.9, 128.6, 127.1, 127.0, 126.8, 126.4, 123.8, 122.9, 121.4, 119.9, 118.4, 113.9, 80.3, 21.0 ppm; IR (KBr): $\tilde{\nu} = 3059$, 3024, 2919, 1632, 1588, 1513, 1461, 1444, 1243, 1222, 1201, 1086, 1003, 803, 749 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max} (ε) = 306 sh (26400), 318 (33500), 333 sh (28400 mol^{-1} dm^3 cm^{-1}); UV (toluene): λ_{max} (ε) = 306 sh (27000), 318 (34800), 333 sh (30000 mol^{-1} dm^3 cm^{-1}); HRMS (MALDI): *m*/*z* (%): calcd for $C_{48}H_{34}O_2S_2$: 706.1995; found: 706.1990 (100) [M^+].

5,5′-Bis[3-(*p*-methoxyphenyl)-[3*H*]-naphtho[2,1-*b*]pyran-3-yl]-2,2′-bithiophene (1e): The general procedure was followed and 2.0 equiv of CuCl$_2$ was used, beige solid was obtained in yield of 65.5%. M.p. 237–238 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.95$ (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 8.5$ Hz, 1H), 7.65 (d, $J = 9.0$ Hz, 1H), 7.52–7.43 (m, 3H), 7.32 (ddd, $J = 8.1$, 6.8, 1.2 Hz, 1H), 7.29 (d, $J = 9.7$ Hz, 1H), 7.16 (d, $J = 8.7$ Hz, 1H), 6.88 (d, $J = 3.7$ Hz, 1H), 6.88–6.82 (m, 2H), 6.79 (d, $J = 3.7$ Hz, 1H), 6.20 (d, $J = 10.0$ Hz, 1H), 3.78 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 159.2$, 150.2, 148.5, 138.1, 136.1, 130.0, 129.7, 129.4, 128.5, 127.7, 127.0, 126.6, 123.7, 122.8, 121.3, 119.8, 118.3, 113.8, 113.4, 80.2, 55.2 ppm; IR (KBr): $\tilde{\nu} = 3055$, 2952, 2838, 1631, 1609, 1586, 1510, 1461, 1439, 1256, 1241, 1177, 1084, 992, 827, 809 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max} (ε) = 306 sh (26900), 318 (34200), 333 sh (29200 mol^{-1} dm^3 cm^{-1}); UV (toluene): λ_{max} (ε) = 306 sh (25700), 318 (33100), 333 sh (28800 mol^{-1} dm^3 cm^{-1}); HRMS (MALDI): *m*/*z* (%): calcd for $C_{48}H_{34}O_4S_2$: 738.1893; found: 738.1893 (100) [M^+].

5,5‴-Bis[3-(*o*-fluorophenyl)-[3*H*]-naphtho[2,1-*b*]pyran-3-yl]-[2,2′,5′,2″,5″,2‴]-quaterthiophene (1f): The general procedure was followed and 1.6 equiv of CuCl$_2$ was used, yellow-green solid was obtained in yield of 76.9%. M.p. 237–238 °C; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 8.00$ (d, $J = 8.1$ Hz, 1H), 7.81 (dt, $J = 7.8$, 1.8 Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.73 (d, $J = 8.7$ Hz, 1H), 7.51 (ddd, $J = 8.4$, 7.2, 1.2 Hz, 1H), 7.40–7.22 (m, 3H), 7.25 (d, $J = 8.7$ Hz, 1H), 7.16 (*dt*, $J = 7.8$, 1.3 Hz, 1H), 7.08 (ddd, $J = 11.3$, 8.1, 1.2 Hz, 1H), 7.04–6.99 (m, 2H), 6.98 (d, $J = 3.7$ Hz, 1H), 6.91 (d, $J = 3.7$ Hz, 1H), 6.49 ppm (dd, $J = 10.0$, 4.4 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 159.0$ ($^{1}J = 248.2$ Hz), 149.7, 146.7, 137.8, 136.0, 135.8, 130.6 ($^{2}J = 10.4$ Hz), 130.0, 129.8 ($^{3}J = 8.5$ Hz), 129.6, 129.5, 128.4, 127.4 ($^{3}J = 2.4$ Hz), 126.8, 126.7, 125.1 ($^{5}J = 4.6$ Hz), 124.3, 124.1, 123.8, 122.9, 121.3, 120.0, 118.0, 116.4 ($^{2}J = 22.0$ Hz), 113.6, 78.2 ppm ($^{3}J = 2.2$ Hz); IR (KBr): $\tilde{\nu} = 3063$, 1632, 1583, 1515, 1484, 1450, 1275, 1230, 1203, 1083, 1005, 809, 794, 756 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max} (ε) = 304 (14300), 318 (17500), 366 sh (28400), 407 (42500 mol^{-1} dm^3 cm^{-1}); UV (toluene): λ_{max} (ε) = 304 (15500), 318 (17900), 366 sh (27600), 407 (40400 mol^{-1} dm^3 cm^{-1}); HRMS (MALDI): *m*/*z* (%): calcd for $C_{62}H_{36}F_2O_2S_4$: 879.1326; found: 879.1320 (100) [M+H$^+$].

5,5‴-Bis[3-(naphthalene-2-yl)-[3*H*]-naphtho[2,1-*b*]pyran-3-yl]-[2,2′,5′,2″,5″,2‴]-quaterthiophene (1g): The general procedure was followed and 1.6 equiv of CuCl$_2$ was used, yellow-green solid was obtained in yield of 88.2%. M.p. 163–165 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.08$ (d, $J = 1.9$ Hz, 1H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.88–7.78 (m, 3H), 7.76–7.64 (m, 3H), 7.54–7.42 (m, 3H), 7.38 (d, $J = 9.6$ Hz, 1H), 7.37–7.30 (m, 1H), 7.27 (d, $J = 9.0$ Hz, 1H), 7.02–6.94 (m, 2H), 6.95 (d, $J = 3.7$ Hz, 1H), 6.88 (d, $J = 3.7$ Hz, 1H), 6.35 ppm (d, $J = 10.0$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 150.2$, 148.2, 141.1, 138.1, 136.1, 135.9, 132.8, 130.1, 129.7, 129.5, 128.5, 128.4, 128.1, 127.5, 127.4, 126.8, 126.6, 126.3, 126.3, 125.2, 124.4, 124.2, 123.8, 122.9, 121.3, 120.3, 118.3, 113.9, 80.4 ppm; IR (KBr): $\tilde{\nu} = 3059$, 2951, 2920, 2867, 1631, 1587, 1514, 1459, 1460, 1437, 1239, 1182, 1084, 1008, 805, 799, 746 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max} (ε) = 304 (17300), 318 (18600), 366 sh (28700), 407 (42700 mol^{-1} dm^3 cm^{-1}); UV (toluene): λ_{max} (ε) = 304 (17400), 318 (18700), 366 sh (28100), 407 (40800 mol^{-1} dm^3 cm^{-1}); HRMS (MALDI): *m*/*z* (%): calcd for $C_{62}H_{38}O_2S_4$: 942.1749; found: 942.1747 (100) [M^+].

5,5‴-Bis[3-(*p*-methoxyphenyl)-[3*H*]-naphtho[2,1-*b*]pyran-3-yl]-[2,2′,5′,2″,5″,2‴]-quaterthiophene (1h): The general procedure was followed and 1.6 equiv of CuCl$_2$ was used, yellow-green solid was obtained in yield of 83.5%. M.p. 230–231 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.98$ (d, $J = 8.3$ Hz, 1H), 7.73 (d, $J = 8.1$ Hz, 1H), 7.68 (d, $J = 9.0$ Hz, 1H), 7.58–7.42 (m, 2H), 7.38–7.31 (m 1H), 7.32 (d, $J = 10.0$ Hz, 1H), 7.20 (d, $J = 8.7$ Hz, 1H), 7.01–6.95 (m, 1H), 6.95 (d, $J = 3.7$ Hz, 1H), 6.93–6.84 (m, 2H), 6.84 (d, $J = 3.7$ Hz, 1H), 6.24 (d, $J = 10.0$ Hz, 1H), 3.79 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 159.2$, 150.2, 148.7, 137.8, 136.1, 136.1, 135.9, 130.0, 129.7, 129.5, 128.5, 127.8, 127.0, 126.9, 126.7, 124.3, 124.2, 123.7, 122.9, 121.3, 119.9, 118.3, 113.8, 113.5, 80.2, 55.3 ppm; IR (KBr): $\tilde{\nu} = 3059$, 2956, 2930, 2834, 1629, 1606, 1584, 1508, 1460, 1440, 1255, 1217, 1171, 1081, 1030, 796, 745 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max} (ε) = 304 (17300), 318 (18600), 366 sh (28700), 407 (42700 mol^{-1} dm^3 cm^{-1}); UV (toluene): λ_{max} (ε) = 304 (17400), 318 (18700), 366 sh (28100), 407 (40800 mol^{-1} dm^3 cm^{-1}); HRMS (MALDI): *m*/*z* (%): calcd for $C_{56}H_{38}O_4S_4$: 902.1647; found: 902.1648 (100) [M^+].

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