Tetrahedron 71 (2015) 4061–4069

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis and sequential photochromism of thiophene-linked bis-pyrans

Xiuhong Lu [a,†], Qian Dong [a,†], Xiaochun Dong [a], Weili Zhao [a,b,*]

[a] School of Pharmacy, Fudan University, Shanghai 201203, PR China
[b] Key Laboratory for Special Functional Materials of the Ministry of Education, Henan University, Kaifeng 475004, PR China

ARTICLE INFO

Article history:
Received 9 March 2015
Received in revised form 16 April 2015
Accepted 20 April 2015
Available online 24 April 2015

Keywords:
Photochromic
Sequential photochromism
Bis-pyrans
Bathochromic
Biphotochromic

ABSTRACT

Novel bis[3*H*]-naphtho[2,1-*b*]pyrans **1a**–**1g** and bis[2*H*]-naphtho[1,2-*b*]pyrans **2a**–**2g** were prepared efficiently. Such thiophene-linked bispyrans display distinct color change under continuous UV irradiation with up to 110 nm of bathochromic shift between the finally generated colored forms and initially generated forms. They also show high colorability, as well as good fatigue-resistance.

1. Introduction

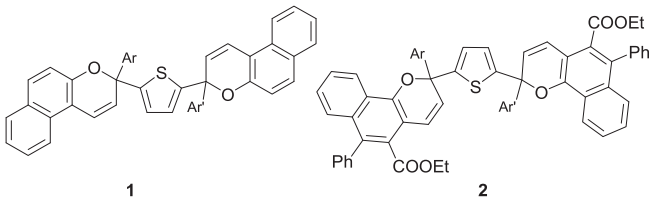
Over the last number of decades, studies on photochromic molecules have become intense areas of research because of their potential applications in information storage, smart windows, optical lenses, optical switches, logic gates, as well as fluorescence modulators.[1,2] There has been recent particular interest in the design, synthesis, and study of novel photochromic dyes containing more than one photochromic unit in a molecule, especially bisphotochromophores in diarylethene,[3] benzodihydropyrene,[4] spiropyran,[5] spirooxazine,[6] diarylpyran,[7,8] as well as hybrid systems.[9] Among the reported bisphotochromic systems, only a few examples existed wherein both photochromic subunits operate synergistically. In the documented bisdiarylethenes, the difference in absorption between the monomeric and dimeric systems is typically less than 20 nm.[3c–g] In unsymmetric bis-dimethyldihydropyrene system, 80 nm difference between biscolored and monocolored forms could be reached, however, the colorability was very low and biscolored forms were generated under laser flash irradiation, and exhibited very fast thermal fading (half-life of 0.1 s at 20 °C).[4] Recently, in hybrid bisphotochromic system involving naphthopyran and diarylethene, the difference of absorption maxima between the final colored forms and that initially generated species upon UV irradiation exceeded 100 nm.[9] However, the diarylethene unit is only photochemically reversible while the pyran system easily undergoes thermal bleaching.

We have documented bisnaphthopyrans displaying sequential and/or temperature-dependent photochromism, as noted by a change in hue with time/temperature under UV irradiation.[8] Bispyrans incorporating a bithiophene linker lead to up to a 62 nm of bathochromic shift between bisopen colored forms and monoopen colored forms generated under UV irradiation.[8b] 1,4-Phenyl linked bispyrans display much shorter absorption (around 430 nm) of the colored forms, however, afford large difference of absorption (up to 60 nm) in temperature-dependent photochromism.[8c] In contrast, 1,3-pheny linked bispyrans provide less distinguishable color change under irradiation.[8c] These results imply that both electronic nature and co-planarity of the bispyrans are crucial to the color change under continuous irradiation. In our continuing interest in the discovery of bisphotochromophores displaying novel properties, on the basis of our earlier observations, we speculate that electron-rich thiophene would be an ideal linker to provide in one hand enough long absorption maxima, in another hand with appropriate distance and co-planarity to allow effective communication between the two open forms, leading to enhanced sequential photochromism. Consequently thiophene-linked bispyrans **1** and **2** were designed and synthesized. For the clear observation of sequential photochromism, the phenyl moieties were substituted with various substituents and furnishes novel systems

* Corresponding author. Tel./fax: +86 21 51980111; e-mail address: zhaoweili@fudan.edu.cn (W. Zhao).
† These authors contribute equally to this work.

http://dx.doi.org/10.1016/j.tet.2015.04.068
0040-4020/

wherein covalently coupled photochromophores work synergistically leading to clear sequential photochromism in both **1** and **2** with greater bathochromic shift (Scheme 1).

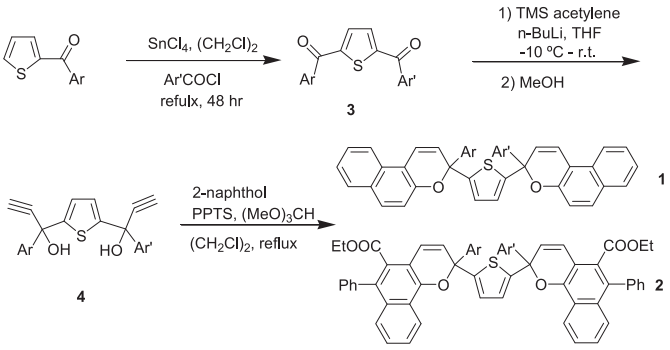


Scheme 1. Molecular structures of photochromic bispyrans **1** and **2**.

2. Results and discussion

2.1. Materials

The syntheses of thiophene-linked bispyrans were shown in Scheme 2. Our synthesis started with easily available aryl thienyl ketone **3**.[8b] For 2,5-diacylthiophene, attempted synthesis following the reported Friedel–Crafts acylation afforded very low yield of the required product.[10] We discovered that by using aroyl chloride as acylating reagent, $SnCl_4$ as Lewis acid and 1,2-dichloroethane as solvent, good yield of diacylthiophene ranging from 43.7% to 84.7% could be obtained. Such a method is also applicable to symmetric bisketone via direct Friedel–Crafts diacylation on thiophene.



a: Ar = Ar' = ph; **b**: Ar = Ar' = *p*-Fph; **c**: Ar = Ar' = *o*-Fph; **d**: Ar = *p*-Fph, Ar' = *o*-Fph; **e**: Ar = Ar' = *p*-Meph; **f**: Ar = Ar' = *p*-MeOph; **g**: Ar = ph, Ar' = *p*-MeOph

Compd	a	b	c	d	e	f	g
3	71.9%	67.8%[a]	52.1%	43.7%	61.2%	71.0%	84.7%
4	73.0%[b]	91.8%	95.9%	97.5%	96.1%	81.3%	91.8%
1	79.7%	82.8%	59.9%	83.7%	86.8%	72.8%	65.1%
2	87.6%	81.9%	69.6%	87.4%	86.7%	79.8%	82.7%

[a]68.5% yield was obtained by direct diacylation on thiophene.

[b]Prepared with sodium acetylide/DMSO/acetylene gas in DMSO.

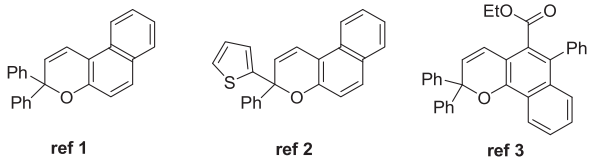
Scheme 2. Synthesis of photochromic bispyrans **1** and **2**.

For bispropargylic alcohol, our modified procedure with sodium acetylide/DMSO/acetylene gas combination, which could reduce the amount of side product significantly was applied successfully for compound **4a** in 73% yield.[8c] Compound **4b**, however, suffered from low yielding and difficult work-up under identical conditions. Thus, alternative way by using lithiated TMS–acetylene in THF, followed by deprotection of TMS with TBAF was developed, which afforded **4b** in excellent yield. Further optimization resulted in a general and synthetic friendly one-pot procedure by adding methanol to the reaction mixture of lithiated TMS–acetylene and bisketone to allow in situ deprotection of TMS group. Excellent yields were obtained for both symmetric and non-symmetric bispropargyl alcohols **4c**–**4g**. Our elegant synthetic procedure with catalytic PPTS and 4 equiv trimethyl orthoformate was adopted for the preparation of the desired bispyrans.[8c,11] Good to excellent yields of thiophene-linked non-symmetric and symmetric bispyrans were obtained.

2.2. Sequential photochromism of compounds 1 and 2

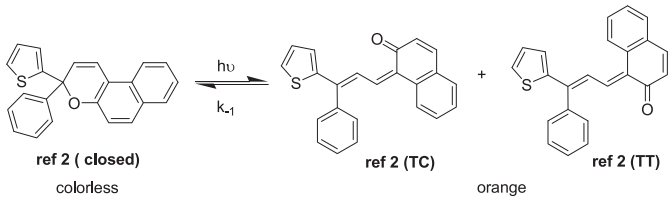
The photochromic properties were typically evaluated by absorption maximum (λ_{max}, maximum wavelength of the colored form), colorability (A_0, the absorbance at photostationary state at absorption maximum under white light irradiation), thermal fading rate (k^{-1}, the bleaching rate of the colored form in the dark), and fatigue-resistance ($T_{1/2}$, time required to decrease to the half of the colorability under white light irradiation).[1]

For the evaluation of photochromic properties of bispyrans **1** and **2**, the photochromic 3,3-diphenyl-[3*H*]-naphtho-[2,1-*b*]pyran (**ref 1**), 3-phenyl-3-thienyl-[3*H*]naphtha [2,1-*b*]pyran (**ref 2**), and 2,6-diphenyl-5-ethoxycarbonyl-2-(thiophene-2-yl)-[2*H*]naphtha [1,2-*b*]pyran (**ref 3**) were used as reference dyes (Scheme 3).[12]



Scheme 3. Molecular structures of reference dyes.

The mechanistic details of the photochromism of the naphthopyrans (e.g., **ref 2**) are shown in Scheme 4. It is well-known that the original state of **ref 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.[13] The TC form has been shown to be generated preferentially in the early stages of the photocoloration process.[14] These (TC and TT) can undergo fast thermal fading, and the bleaching process can be enhanced photochemically with visible light.



Scheme 4. Photochromic reaction of **ref 2**.

All the synthesized bispyrans **1a**–**1g** and **2a**–**2g** display sequential and/or temperature-dependent photochromism as expected. As typical examples, the color and absorption spectra of **1c** and **2c** prior to and after UV irradiation are shown in Fig. 1. The colorless solution of **1c** in toluene displays four distinct absorption

peaks located in the region 300–400 nm, which are 304, 317, 347, and 361 nm, respectively. Upon UV irradiation, a yellow color was generated quickly. Under prolonged exposure to UV irradiation, the color hue started change from yellow to red and finally to purple. For bispyran **2c**, the slightly pale pink solution turned red (λ_{max}=494 nm), then purple, and finally blue (λ_{max}=606 nm) upon UV (366 nm) irradiation. In both cases, greater than 100 nm of bathochromic shift between final generated colored forms and initial colored forms were observed, and the absorption spectra of those colored forms was found to cover the entire visible region. These distinct color hue changes are attributed to the photochemical opening of the second photochromic unit, which renders extended conjugation and exhibits color hue change.

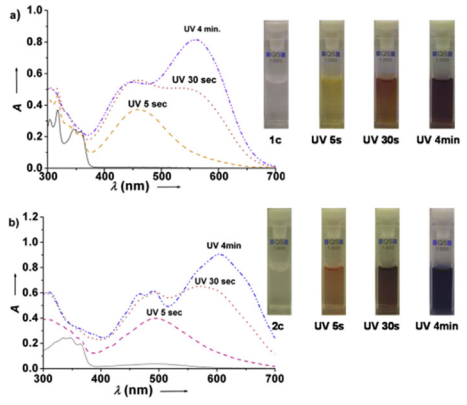
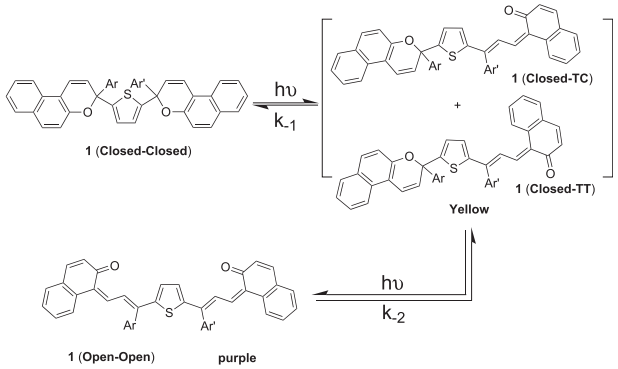


Fig. 1. UV–visible spectra of 2.5×10^{-5} M solution of bispyran **1c** (top) and **2c** (bottom) prior to and after UV (366 nm) irradiation at room temperature, respectively.

2.3. Photocoloration and quantum yield measurements

We believe such TC and TT isomers are generated during the sequential photochromism of **1** and **2** as well.

The photochromic process involving bispyran **1** is shown in Scheme 4. The original state of **1** is the closed–closed form (Closed-Closed); upon UV irradiation, one pyran unit opens to generate closed-open forms, which constitute the fast-fading closed-trans-cis isomer (Closed-TC) and slow fading closed-trans-trans isomer (Closed TT), which display yellow color accordingly. Under extended UV irradiation, the second pyran unit undergoes opening to generate open–open forms (Open-Open, only one isomer is shown in Scheme 5), which display purple color.



Scheme 5. Photochromic reactions of bispyran **1**.

We proceeded to identify the colored species generated with **1a** after short time UV irradiation for monocolored Closed-TC and Closed-TT forms by taking advantage the relatively long lifetime of the colored forms at low temperature. The implementation of low-temperature chromatography technique allows us to isolate pure and Closed-TT of **1a** (Fig. 2).[8b] Once warmed up to room temperature, the colored form(s) converted to the colorless closed–closed form and allowed the calculated absorption coefficients ε (dm^{-3} mol^{-1} cm^{-1}) for Closed-TC as 304 (19,600), 318 (20,200), 337sh (14,100), and 478 (22,200).[8b] For Closed-TT, the absorption coefficients are 303 (17,800), 317 (17,800), 337sh (12,700), and 479 (19,500).[8b]

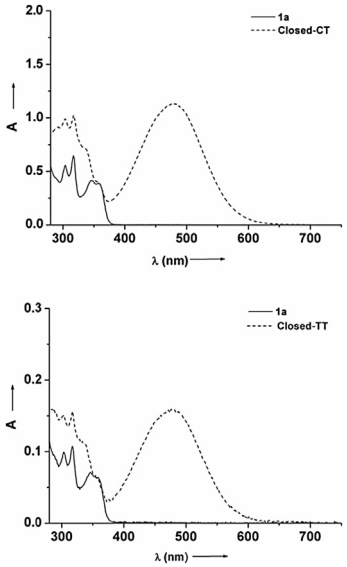


Fig. 2. Absorption spectra of the colored species of **1a** isolated by low-temperature chromatography on silica gel at −78 °C in dichloromethane.

Similarly, the Closed-TC of the colored species of **2a** was isolated as well and the absorption coefficients ε (dm^{-3} mol^{-1} cm^{-1}) were calculated to be 313 (21,200), 333 (15,300), 348 (13,700), 365 (10,500), and 509 (15,800).

Due to the co-existence of various colored species under prolonged irradiation and relatively fast fading of the open–open isomers, the attempted isolation of the long wavelength closed–closed isomers as clean species was unsuccessful.

Photocoloration kinetic measurements were carried out in thermostated cuvette irradiated with UV (366 nm) 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 to be 7.98×10^{-6} E s^{-1} dm^{-3}.[15]

In general biexponential fading processes are involved for photochromic pyrans. Upon short period time of irradiation ($t\leq6$ s), due to the low content of slow fading Closed-TT, the fading process is dominated by Closed-TC and could be simplified as monoexponential process.[14] Thus the photochromic reaction is simplified as:

$$\text{Closed-Closed} \underset{k_{-1}}{\overset{\Phi}{\rightleftharpoons}} \text{Closed-TC}$$

The following equation could be obtained from the literature:[16]

$$dA_{\text{Closed-TC}}/dt = \varepsilon_{\text{Closed-TC}}\Phi I_0[1-\exp(-2.3A_{\text{Closed-Closed}})] - k^{-1}A_{\text{Closed-TC}}$$

The quantum efficiency Φ could be calculated by the following equation: $\Phi=(dA_{\text{Closed-TC}}/dt)_{t\to 0}/\{\varepsilon_{\text{Closed-TC}} I_0[1-\exp(-2.3 A_{\text{Closed-Closed}})]\}$. Wherein $A_{\text{Closed-TC}}$ is the absorbance of Closed-TC at absorption maximum. $\varepsilon_{\text{Closed-TC}}$ is the absorption coefficient of Closed-TC; I_0 is the intensity of the light. $A_{\text{Closed-Closed}}$ is the absorbance of Closed–Closed at the irradiation wavelength (366 nm). $(dA_{\text{Closed-TC}}/dt)_{t\to 0}$ could be obtained from linear fitting of photocoloration curve.[8b]

By applying the obtained data from Fig. 3, the photocoloration quantum yields were calculated. Repetition of three parallel measurements allowed the determination of Φ as 0.74±0.01 for **1a** and 0.98±0.01 for **2a**, respectively (see Supplementary data for details). The reference dye **ref 1** possesses the quantum yield of 0.92. Thus very efficient process of coloration took place among the bispyrans.

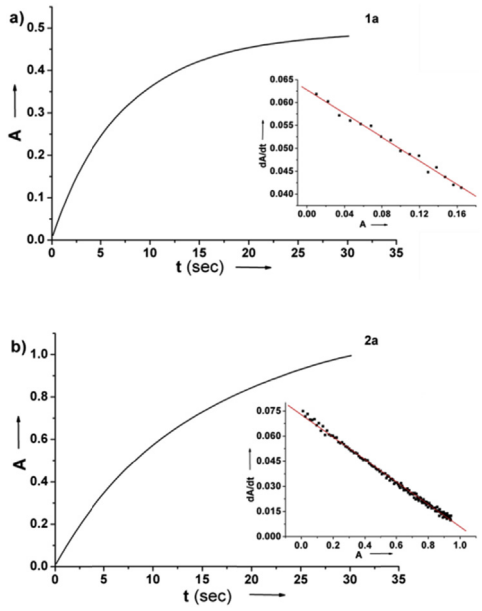


Fig. 3. Photocoloration of compound **1a** (a) and **2a** (b) in CH_2Cl_2 (5×10^{-5} M) at 300 K upon UV irradiation (monitored at 478 nm for **1a** and 509 nm for **2a**, respectively). Inset: linear fit of the coloring kinetics.

2.4. Colorability of compounds 1 and 2 and thermal fading of the colored forms

Due to the complication involved in bisphotochromic processes, we only studied the thermal fading of one of the initial formed monocolored forms. 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 thermo-cryostat to be 287.4 K.

Mathematic manipulation of the curve in Fig. 4 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 0.107 s^{-1} at 298.4 K.

2.5. Fatigue-resistance measurements

The fatigue-resistance of photochromic compound was measured by monitoring the absorbance of a continuous irradiated solution of photochromic compound in toluene with white light with UV–vis spectrometer (see Supplementary data for details). Examples were shown in Fig. 5 for compounds **1a** and **2a** in comparison with **ref 1** dye.

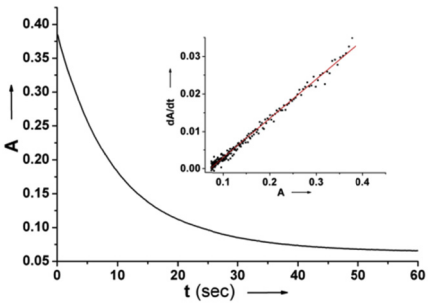


Fig. 4. Thermodecoloration of Closed-TC of compound **1a** in toluene (5×10^{-5} M) at 298.4 K monitored at 478 nm. Inset: linear fit.

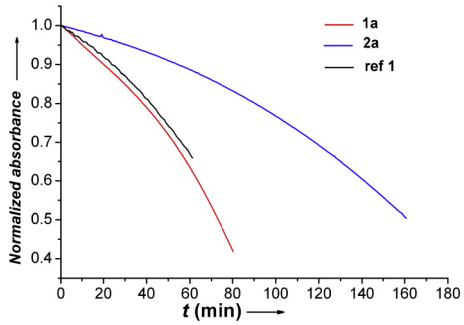


Fig. 5. Normalized absorbance of photochromic compound under continuous irradiation with xenon lamp.

Other photochromic compounds were measured as well. The summary of the photochromic properties was collected in Table 1. The half-life of the bispyrans well collected in Table 1. The colorability, thermal fading rate were included as well.

Table 1
Colorability (A_0), absorption maxima, thermal fading rate (k^{-1}), and fatigue-resistance ($T_{1/2}$) of bispyrans at 298.4 K in toluene

Compd	Ar	Ar′	A_0/λ_{max} (nm)	k^{-1} (s^{-1})	$T_{1/2}$ (min)
1a	Ph	Ph	0.391/468	0.107	108
1b	*p*-Fph	*p*-Fph	0.308/466	0.163	113
1c	*o*-Fph	*o*-Fph	0.536/460	0.025	73
1d	*p*-Fph	*o*-Fph	0.529/455	0.084	94
1e	*p*-Meph	*p*-Meph	0.315/476	0.149	120
1f	*p*-MeOph	*p*-MeOph	0.243/487	0.252	155[a]
1g	Ph	*p*-MeOph	0.295/483	0.179	122
2a	Ph	Ph	0.681/494	0.015	218[a]
2b	*p*-Fph	*p*-Fph	0.686/494	0.019	234
2c	*o*-Fph	*o*-Fph	0.699/494	0.004	161
2d	*p*-Fph	*o*-Fph	0.694/494	0.012	179
2e	*p*-Meph	*p*-Meph	0.692/494	0.020	223[a]
2f	*p*-MeOph	*p*-MeOph	0.672/494	0.035	237[a]
2g	Ph	*p*-MeOph	0.707/495	0.025	216[a]
ref 1			0.390/432	0.101	85
ref 2			0.275/478	0.126	137[a]
ref 3			0.542/505	0.023	342[a]

[a] Estimated from 1 h experimental result.

From Table 1, it could be concluded that all the bispyrans possess very high colorability. The bispyrans display greater colorability, higher fading rate, however diminished fatigue-resistance than corresponding pyran precursors (compare **1a** with **ref 2**, **2a** with **ref 3**).

The substituent in the phenyl ring of the bispyran dye has significant effects on the photochromic properties, which follows the same trend as the monophotochromic pyran system.[1] Moreover,

the pattern of the substitution affects the sequential photochromism significantly in the bispyrans. Fluorine substitution on the 3-phenyl group has little effect on the absorption maxima of the colored form, however, it affects thermal fading rate. *para*-Fluoro substitution led to increased fading rate and enhanced fatigue-resistance (**1b**, **2b** in comparison with **1a**, **2a**). *ortho*-Fluoro substitution, however, resulted in significantly decreased thermal fading rate, diminished fatigue-resistance (**1c**, **1d**, **2c**, **2d**). Electron donating substituent decreases colorability and concurrently increases the fading rate, as well as fatigue-resistance (**1e**–**1g**, **2e**–**2g**). Bispyran substituted with *para*-methoxyphenyl shows temperature-dependent photochromism and affords the highest fading rate, the best fatigue-resistance, however, with the poorest colorability (**1f**, **2f**).

3. Conclusion

In conclusion, bis[3*H*]-naphtho[2,1-*b*]pyran **1** and bis[2*H*]-naphtho[1,2-*b*]pyran **2** represent unique dimeric systems possessing sequential photochromic properties. Compounds **1** and **2** possess high colorability and good fatigue-resistance. More interestingly, bathochromic shifts greater than 100 nm were observed in the studied sequential photochromic process. The high colorability, good fatigue-resistance, broad absorption, and tunable color change upon UV irradiation may render the bispyrans as novel photochromic dyes for the preparation of materials with applications in display, filter, and modulation of fluorescence.

4. Experimental section

4.1. General procedure for preparation of diacyl-thiophenes (3)

Aroyl chloride (10.5 mmol), thiophene-2-yl aryl ketone (10 mmol), and tin chloride (10.5 mmol) were refluxed in 1,2-dichloroethane for 24 h. The cooled reaction mixture was poured into a mixture of ice (50 g) and 5 M HCl (5 ml) with vigorous stirring. Extracted with methylene chloride, filtrated through a pad of silica gel, wash with methylene chloride, and decolored with charcoal. Solvent was removed, the residue was recrystallized from methylene chloride/ethanol. Solid was collected by filtration. The mother liquid was concentrated to dryness, purified by chromatography (silica gel, methylene chloride/hexane=2:3 as eluant) and recrystallization from ethanol.

*4.1.1. 2,5-Dibenzoyl-thiophene (**3a**).* The general procedure was followed and pale-yellow-gray solid was obtained in yield of 71.9%. Mp 112–113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.95–7.85 (4H, m), 7.68 (2H, s), 7.68–7.60 (m, 2H), 7.58–7.48 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=188.3, 148.6, 137.4, 133.8, 133.1, 129.4, 128.7 ppm; IR ($CHCl_3$): ν_{max}=3012, 1644, 1600, 1579, 1516, 1448, 1340, 1318, 1276, 1258, 1220, 1180, 1127, 880 cm^{-1}.

*4.1.2. 2,5-Di(p-fluorobenzoyl)thiophene (**3b**).* The general procedure was followed and pale-yellow solid was obtained in yield of 67.8%. Mp 184.8–186.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.00–7.92 (m, 4H), 7.67 (s, 2H), 7.28–7.17 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=186.4, 165.6 (^1J=255.1 Hz), 148.2, 133.5, 133.4 (^4J=2.4 Hz), 131.9 (^3J=7.6 Hz), 115.8 ppm (^2J=22.0 Hz); IR ($CHCl_3$): ν_{max}=3022, 1645, 1600, 1506, 1409, 1339, 1276, 1242, 1156, 887, 850 cm^{-1}.

*4.1.3. 2,5-Di(o-fluorobenzoyl)thiophene (**3c**).* The general procedure was followed and pale-yellow solid was obtained in yield of 52.1%. Mp 111–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.24 (t, J=1.6 Hz, 1H), 7.98–7.94 (m, 1H), 7.66–7.50 (m, 5H), 7.33–7.14 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=185.8, 184.8, 159.62 (^1J=252.1 Hz), 159.57 (^1J=252.1 Hz), 144.6, 142.3, 141.9 (^5J=2.4 Hz), 134.7 (^5J=2.4 Hz), 134.1 (^2J=3.1 Hz), 133.46 (^3J=8.5 Hz), 133.43 (^3J=8.5 Hz), 130.3 (^3J=2.4 Hz), 130.2 (^3J=2.4 Hz), 126.7 (^2J=14.7 Hz), 126.1 (^2J=14.7 Hz), 124.4 (^4J=3.7 Hz), 124.3 (^4J=3.7 Hz), 116.5 (^2J=21.4 Hz), 116.4 ppm (^2J=21.4 Hz).

*4.1.4. 2-(o-Fluorobenzoyl)-5-(p-fluorobenzoyl)thiophene (**3d**).* The general procedure was followed except that the refluxing time was 26.5 h and pale-yellow solid was obtained in yield of 43.7%. Mp 136.2–137.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.24 (t, J=1.6 Hz, 0.5H), 8.04 (t, J=1.0 Hz, 0.5H), 7.98–7.91 (m, 2H), 7.66–7.50 (m, 3H), 7.33–7.14 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=186.2, 186.2, 185.9, 165.9 (^1J=254.5 Hz), 159.6 (^1J=247.0 Hz), 148.8, 144.1, 142.1, 141.2 (^5J=2.4 Hz), 134.0 (^5J=2.9 Hz), 133.8, 133.6, 133.6, 133.5, 133.5, 133.5, 133.3 (^2J=8.7 Hz), 133.2 (^2J=8.7 Hz), 132.0, 131.8, 131.7, 130.31 (^3J=2.5 Hz), 133.2 (^3J=2.5 Hz), 126.8, 126.6, 126.3, 124.4 (^4J=3.7 Hz), 124.3 (^4J=3.7 Hz), 116.6 (^2J=21.4 Hz), 116.4 (^2J=21.4 Hz), 115.9 ppm (^2J=22.0 Hz); IR ($CHCl_3$): ν_{max}=3022, 1647, 1612, 1601, 1519, 1507, 1486, 1454, 1300, 1280, 1242, 1218, 1097, 890, 874, 850 cm^{-1}.

*4.1.5. 2,5-Di(p-methylbenzoyl)thiophene (**3e**).* The general procedure was followed and pale-yellow solid was obtained in yield of 61.2%. Mp 143–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.89–7.80 (m, 4H), 7.67 (s, 2H), 7.36–7.29 (m, 4H), 2.46 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=187.7, 148.4, 143.9, 134.6, 133.4, 129.6, 129.3, 21.7 ppm. IR ($CHCl_3$): ν_{max}=3027, 3020, 3013, 2925, 1640, 1607, 1570, 1517, 1443, 1408, 1340, 1312, 1278, 1261, 1182, 1125, 1020, 911, 886, 835 cm^{-1}.

*4.1.6. 2,5-Di(p-methoxybenzoyl)thiophene (**3f**).* The general procedure was followed and yellow solid was obtained in yield of 84.7%. Mp 192.5–193.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.99–7.91 (m, 4H), 7.66 (s, 2H), 7.06–6.94 (m, 4H), 3.91 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=186.3, 163.4, 148.1, 132.8, 131.7, 129.8, 113.8, 55.6 ppm. IR ($CHCl_3$): ν_{max}=3020, 2938, 2843, 1636, 1601, 1574, 1509, 1463, 1442, 1420, 1310, 1282, 1257, 1172, 1030, 896, 845 cm^{-1}.

*4.1.7. 2-Benzoyl-5-(p-methoxylbenzoyl)thiophene (**3g**).* The general procedure was followed and pale-yellow solid was obtained in yield of 71.0%. Mp 151–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.99–7.93 (m, 2H), 7.93–7.88 (m, 2H), 7.70–7.60 (m, 3H), 7.58–7.49 (m, 2H), 7.05–6.98 (m, 2H), 3.91 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=187.9, 186.3, 163.5, 148.8, 147.6, 137.2, 133.6, 132.9, 132.8, 131.9, 131.8, 129.7, 129.2, 128.5, 113.8, 55.6 ppm; IR ($CHCl_3$): ν_{max}=3022, 2938, 2842, 1640, 1574, 1510, 1461, 1442, 1420, 1340, 1311, 1278, 1258, 1174, 1127, 1029, 910, 884, 845 cm^{-1}.

4.2. Direct bisacylation for the synthesis of bisketone 3b

Tin chloride (17 mmol) was added dropwise with stirring to a mixture of *p*-fluorobenzoyl chloride (17 mmol) and thiophene (8 mmol) in dry 1,2-dichloroethane at 0–5 °C over 10 min, stirred for 2 h. Then the mixture was refluxed for 48 h, cooled down, poured into a mixture of ice (50 g) and 5 M HCl (5 ml) under vigorous stirring. The mixture was extracted with dichloromethane, filtrated through a pad of silica gel, and washed with dichloromethane. Most of the solvents were removed in vacuo, the resulted solid was filtered, recrystallized from dichloromethane/hexane. Solid was collected by filtration. The mother liquid was concentrated to dryness, digested with dichloromethane/hexane, and then recrystallized from dichloromethane/hexane. **3b** was obtained in yield of 68.5%.

*4.2.1. 1,4-Di(1-hydroxy-1-phenyl-prop-2-ynyl)thiophene (**4a**).* Bisketone **3a** (1.65 g, 5.65 mmol) was added in one portion to a suspension of sodium acetylide (1.09 g, 22.67 mmol) in dry THF

(20 ml) with stirring while acetylene gas was bubbled. DMSO (5 ml) was added. The mixture was stirred at room temperature for 3 h while keeping bubbling of acetylene. The mixture was allowed to stir overnight, poured onto crush ice, and extracted with dichloromethane. After removal of solvent, the residue was purified by chromatography and by recrystallization from dichloromethane/hexane to afford **4a** in yield of 73% as pale-yellow gel. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.71–7.64 (m, 4H), 7.40–7.30 (m, 6H), 6.89 (s, 1H), 6.85 (s, 1H), 2.93 (s, 2H), 2.87 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=149.9, 143.2, 143.1, 128.3, 125.7, 125.6, 124.9, 124.9, 85.4, 75.1, 75.1, 71.7 ppm; IR ($CHCl_3$): ν_{max}=3582, 3306, 3066, 3013, 2927, 1490, 1450, 1179, 1031, 974, 868, 813 cm^{-1}.

4.3. General procedure for preparation of bispropargylic alcohols (4)

Butyl lithium (1.6 M in hexane, 11 mmol) was added over 1 min to a solution of TMS–acetylene (1.55 ml, 11 mmol) in THF (15 ml) at −10 °C with stirring, the mixture was stirred for 10 min, 2,5-di(*o*-fluorobenzoyl)thiophene (1.65 g, 5 mmol) was added in one portion, stirred for over 0.5 h, warmed up to room temperature, and stirred over night. Methanol (8 ml) was added, stirred for 2 h before water (20 ml) was added. The reaction mixture was neutralized with 5 M HCl to pH about 6, extracted with ethyl acetate, dried with anhydrous sodium sulfate, and filtered. After removal of solvent, the resulted oil was purified by chromatography on silica gel (ethyl acetate/hexane=1:3 as eluant), dried in high vacuum. Bispropargyl alcohol derivative was obtained as pale-yellow gel, which was used directly into the next step without further purification.

*4.3.1. 2,5-Di(1-hydroxy-1-phenyl-prop-2-ynyl)thiophene (**4a**).* The general procedure was followed. Compound **4a** was obtained in yield of 92.9% as pale-yellow gel, which solidified on standing in a refrigerator.

*4.3.2. 2,5-Di[1-hydroxy-1-(p-fluorophenyl)-prop-2-ynyl]thiophene (**4b**).* The general procedure was followed and yellow-brown gel was obtained in yield of 91.8%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.69–7.59 (m, 4H), 7.08–6.98 (m, 4H), 6.89 (s, 1H), 6.86 (s, 1H), 2.96 (s, 2H), 2.88 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=162.3 (^1J=247.2 Hz), 149.9, 149.8, 138.93 (^4J=4.9 Hz), 138.87 (^4J=4.9 Hz), 127.54 (^3J=8.6 Hz), 127.49 (^3J=8.4 Hz), 124.8, 115.0 (^2J=20.0 Hz), 85.1, 75.4, 71.2 ppm; ^{19}F NMR (300 MHz, $CDCl_3$): δ=−113.6 ppm; IR ($CHCl_3$): ν_{max}=3582, 3306, 3020, 1604, 1508, 1226, 1159, 1033, 975, 835 cm^{-1}.

*4.3.3. 2,5-Di[1-hydroxy-1-(o-fluorophenyl)-prop-2-ynyl]thiophene (**4c**).* The general procedure was followed and pale-yellow gel was obtained in yield of 95.9%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.72–7.62 (m, 2H), 7.39–7.29 (m, 2H), 7.17 (td, *J*=7.6, 1.6 Hz, 1H), 7.15 (td, *J*=7.6, 1.6 Hz, 1H), 7.07 (td, *J*=8.1, 1.2 Hz, 1H), 7.03 (td, *J*=8.1, 1.2 Hz, 1H), 7.00 (s, 1H), 6.95 (s, 1H), 3.24 (d, *J*=2.2 Hz, 1H), 3.23 (*J*=2.2 Hz, 1H), 2.85 (s, 1H), 2.85 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.72 (^1J=249.0 Hz), 159.68 (^1J=249.0 Hz), 148.2, 148.4, 130.2 (^3J=7.9 Hz), 126.98 (^3J=8.8 Hz), 126.94 (^3J=8.8 Hz), 125.0, 123.8 (^4J=3.7 Hz), 116.2 (^2J=22.0 Hz), 83.8, 83.8, 74.64 (^5J=2.2 Hz), 74.58 (^5J=2.3 Hz), 68.9, 68.9 ppm; ^{19}F NMR (300 MHz, $CDCl_3$): δ=−110.6 ppm; IR ($CHCl_3$): ν_{max}=3586, 3306, 3013, 1614, 1490, 1450, 1179, 1031, 974, 868, 813 cm^{-1}.

*4.3.4. 2-[1-Hydroxy-1-(o-fluorophenyl)-prop-2-ynyl]-5-[1-hydroxy-1-(p-fluorophenyl)-prop-2-ynyl] thiophene (**4d**).* The general procedure was followed and pale-yellow gel was obtained in yield of 97.5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.74–7.59 (m, 3H), 7.39–7.29 (m, 1H), 7.20–7.12 (m, 1H), 7.10–6.97 (m, 3H), 6.91–6.87 (m, 2H), 3.22 (t, *J*=3.2 Hz, 1H), 2.97 (s, 1H), 2.88 (d, *J*=0.9 Hz, 1H), 2.85 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=162.3 (^1J=246.6 Hz), 126.98 (^1J=249.0 Hz), 149.7, 149.7, 148.3, 148.3, 138.99 (^4J=4.9 Hz), 138.94 (^4J=4.9 Hz), 130.32 (^3J=8.6 Hz), 127.50 (^3J=7.9 Hz), 127.49 (^3J=8.5 Hz), 126.96 (^3J=7.1 Hz), 126.93 (^3J=7.1 Hz), 125.0, 123.8 (^4J=3.7 Hz), 116.3 (^2J=21.4 Hz), 115.0 (^2J=21.4 Hz), 85.1, 85.0, 83.8, 83.8, 75.3, 75.3, 74.72 (^5J=2.2 Hz), 74.67 (^5J=2.2 Hz), 71.2, 69.0, 68.9 ppm; ^{19}F NMR (300 MHz, $CDCl_3$): δ=−110.6, −113.7 ppm; IR ($CHCl_3$): ν_{max}=3586, 3306, 3013, 1614, 1490, 1450, 1179, 1031, 974, 868, 813 cm^{-1}.

*4.3.5. 2,5-Di[1-hydroxy-1-(p-methylphenyl)-prop-2-ynyl]thiophene (**4e**).* The general procedure was followed and pale orange gel was obtained in yield of 96.1%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.59–7.51 (m, 4H), 7.20–7.12 (m, 4H), 6.89 (s, 1H), 6.84 (s, 1H), 2.89 (s, 2H), 2.85 (s, 2H), 2.35 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=149.8, 140.3, 138.0, 128.9, 125.5, 125.5, 124.7, 85.5, 74.9, 71.6, 21.2 ppm; IR ($CHCl_3$): ν_{max}=3581, 3306, 3022, 2925, 2871, 1511, 1454, 1408, 1375, 1330, 1250, 1182, 1034, 974, 873, 817 cm^{-1}.

*4.3.6. 2-[1-Hydroxy-1-(p-methoxyphenyl)-prop-2-ynyl]-5-(1-hydroxy-1-(p-methylphenyl)-prop-2-ynyl)thiophene (**4g**).* The general procedure was followed and pale orange gel was obtained in yield of 91.8%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.70–7.64 (m, 2H), 7.62–7.55 (m, 2H), 7.40–7.28 (m, 3H), 6.92–6.82 (m, 4H), 3.81 (s, 3H), 2.96 (s, 1H), 2.91 (s, 1H), 2.87 (s, 1H), 2.86 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.2, 150.1, 149.6, 143.0, 135.3, 128.2, 128.1, 127.0, 126.9, 125.6, 125.5, 124.7, 124.6, 113.5, 85.6, 75.1, 75.0, 71.7, 71.4, 55.3 ppm; IR ($CHCl_3$): ν_{max}=3581, 3305, 3020, 1608, 1510, 1450, 1252, 1177, 1035, 973, 870, 828 cm^{-1}.

*4.3.7. 2,5-Di[1-hydroxy-1-(p-methoxyphenyl)-prop-2-ynyl]thiophene (**4f**).* Butyl lithium (1.6 M in hexane, 6.7 mmol) was added over 10 min to a solution of TMS–acetylene (0.94 ml, 6.6 mmol) in THF (10 ml) at −10 °C with stirring, the mixture was stirred for 0.5 h, then ketone was added in one portion, stirred for over 0.5 h, warmed up to room temperature, and stirred over night. Aqueous ammonium chloride solution was used to quench the reaction, and ethyl acetate was used to extract product. Removal of solvent provided brown oil, which was used directly for the next step.

Such brown oil was dissolved in THF and was treated with TBAF (1 M in THF, 8 ml) at 0–5 °C, then stirred at room temperature for 1 h. The reaction mixture was quenched with water and extracted with ethyl acetate, removal of solvent afforded fairly pure **4f** as orange gel in yield of 81.3%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.62–7.54 (m, 4H), 6.91–6.82 (m, 4H), 6.88 (s, 1H), 6.84 (s, 1H), 3.81 (s, 6H), 2.92 (s, 2H), 2.86 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.3, 149.9, 135.4, 127.0, 126.9, 124.6, 113.5, 85.5, 74.9, 71.4, 55.3 ppm; IR ($CHCl_3$): ν_{max}=3581, 3305, 3018, 3012, 2960, 2840, 1608, 1510, 1460, 1176, 1036, 973, 830 cm^{-1}.

4.4. General procedure for preparation of bispyrans (1 and 2)

Bispropargyl alcohol (0.5 mmol), 2-naphthol (1.05 mmol), PPTS (13.4 mg, 0.05 mmol), and trimethyl orthoformate (0.21 ml, 2.0 mmol) in 1,2-dichloroethane (2 ml) were refluxed for 2–3 h, filtered through a pad of alumina while it was hot, and washed with 1,2-dichloroethane. The filtrate was concentrated, recrystallized from dichloromethane/hexane. The solid was collected by filtration. The mother liquid was concentrated and purified by chromatography (silica gel). Recrystallization (dichloromethane/hexane) afforded bispyran.

*4.4.1. 2,5-Di-(3-phenyl-[3H]-naphtho[2,1-b]pyran-3-yl)-thiophene (**1a**).* The general procedure was followed and pale pink solid was obtained in yield of 79.7%. Mp 213–214 °C; ^{1}H NMR (300 MHz,

$CDCl_3$): δ=7.93 (d, J=8.1 Hz, 2H), 7.73 (d, J=8.1 Hz, 2H), 7.65 (dd, J=9.0, 2.2 Hz, 2H), 7.64–7.55 (m, 4H), 7.53–7.43 (m, 2H), 7.40–7.18 (m, 12H), 6.73 (d, J=2.5 Hz, 2H), 6.27 ppm (d, J=10.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=150.2, 150.2, 143.9, 129.9, 129.7, 129.4, 128.5, 128.0, 127.8, 126.9, 126.6, 126.3, 125.6, 125.5, 123.6, 121.3, 119.6, 118.2, 113.6, 80.4, 80.3 ppm. IR (KBr): ν_{max}=3059, 1633, 1589, 1515, 1460, 1384, 1245, 1204, 1090, 1006, 812, 740 cm^{-1}. HRMS (MALDI) calcd for $C_{42}H_{28}O_2S$: m/z (%): 619.1702 $[M+Na]^+$. Found: 619.1709 (32.4%).

*4.4.2. 2,5-Di-[3-(p-fluorophenyl)-[3H]-naphtho[2,1-b]pyran-3-yl]-thiophene (**1b**).* The general procedure was followed and pale pink solid was obtained in yield of 82.8%. Mp 198.5–200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.94 (d, J=8.7 Hz, 2H), 7.72 (d, J=8.1 Hz, 2H), 7.66 (dd, J=9.0, 1.9 Hz, 2H), 7.56–7.43 (m, 6H), 7.38–7.27 (m, 3H), 7.15 (dd, J=8.7, 3.7 Hz, 2H), 7.03–6.93 (m, 4H), 6.68 (d, J=1.2 Hz, 2H), 6.20 ppm (d, J=9.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=162.2 (^1J=246.6 Hz), 150.0, 149.9, 139.5 (^4J=2.4 Hz), 130.0, 129.6, 129.3, 128.4, 128.18 (^3J=8.4 Hz), 128.15 (^3J=8.4 Hz), 126.7, 126.5, 125.5, 125.4, 123.7, 121.2, 119.8, 118.1, 114.8 (^2J=21.4 Hz), 113.6, 80.0, 80.0 ppm. IR (KBr): ν_{max}=3061, 1634, 1601, 1586, 1506, 1460, 1384, 1229, 1205, 1157, 1084, 996, 952, 828, 816, 749 cm^{-1}. HRMS (MALDI) calcd for $C_{42}H_{26}F_2O_2S$: m/z (%): 655.1514 $[M+Na]^+$. Found: 655.1509 (58.1%).

*4.4.3. 2,5-Di-[3-(o-fluorophenyl)-[3H]-naphtho[2,1-b]pyran-3-yl]-thiophene (**1c**).* The general procedure was followed and pale pink solid was obtained in yield of 59.9%. Mp 178–180.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.92 (d, J=8.4 Hz, 2H), 7.72 (d, J=7.8 Hz, 2H), 7.70 (d, J=8.1 Hz, 2H), 7.67 (d, J=8.4 Hz, 2H), 7.50–7.42 (m, 2H), 7.37–7.28 (m, 2H), 7.28–7.19 (m, 6H), 7.11–6.96 (m, 4H), 6.74 (s, 2H), 6.46 (d, J=10.0 Hz, 1H), 6.44 ppm (d, J=10.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.2 (^1J=248.4 Hz), 149.8, 148.9, 130.6 (^2J=11.0 Hz), 130.0, 129.8 (^3J=8.6 Hz), 129.7, 129.5, 128.5, 127.6 (^3J=2.4 Hz), 126.7, 125.6, 125.6, 125.3, 123.8, 123.7 (^4J=3.1 Hz), 121.4, 119.5, 118.1, 116.5 (^2J=22.6 Hz), 113.6, 78.5, 78.5 ppm. IR (KBr): ν_{max}=3058, 1634, 1615, 1583, 1515, 1484, 1448, 1385, 1276, 1246, 1229, 1215, 1108, 1084, 1006, 913, 807, 748 cm^{-1}. HRMS (MALDI) calcd for $C_{42}H_{26}F_2O_2S$: m/z (%): 655.1514 $[M+Na]^+$. Found: 655.1508 (64.3%).

*4.4.4. 2-[3-(o-Fluorophenyl)-[3H]-naphtho[2,1-b]pyran-3-yl]-5-[3-(p-fluorophenyl)-[3H]-naphtho[2,1-b]pyran-3-yl]-thiophene (**1d**).* The general procedure was followed and pale pink solid was obtained in yield of 83.7%. Mp 166–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.93 (d, J=8.7 Hz, 2H), 7.78–7.60 (m, 5H), 7.57–7.42 (m, 4H), 7.38–7.20 (m, 6H), 7.20–7.02 (m, 6H), 6.78–6.64 (m, 2H), 6.46 (d, J=10.0 Hz, 0.5H), 6.44 (d, J=10.0 Hz, 0.5H), 6.24–6.17 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=162.1 (^1J=246.0 Hz), 159.0 (^1J=248.4 Hz), 149.9, 149.9, 149.7, 148.9, 139.5 (^4J=2.4 Hz), 130.5 (^2J=11.0 Hz), 129.9, 129.9, 129.7 (^3J=8.6 Hz), 129.6, 129.4, 129.3, 128.2 (^3J=8.4 Hz), 128.2 (^3J=8.4 Hz), 127.5 (^3J=1.9 Hz), 126.6, 126.6, 125.5, 125.4, 125.4, 125.2, 123.7 (^4J=4.9 Hz), 121.2, 121.2, 119.7, 119.5, 118.1, 118.0, 116.4 (^2J=22.0 Hz), 114.8 (^2J=22.0 Hz), 113.5, 80.0, 80.0, 78.4, 78.4 ppm. IR (KBr): ν_{max}=3059, 1634, 1603, 1586, 1504, 1482, 1459, 1384, 1270, 1232, 1203, 1156, 1083, 996, 953, 827, 817, 751 cm^{-1}. HRMS (MALDI) calcd for $C_{42}H_{26}F_2O_2S$: m/z (%): 655.1514 $[M+Na]^+$. Found: 655.1520 (53.9%).

*4.4.5. 2,5-Di-[3-(p-methylphenyl)-[3H]-naphtho[2,1-b]pyran-3-yl]-thiophene (**1e**).* The general procedure was followed and pale pink solid was obtained in yield of 86.8%. Mp 222–223 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.92 (d, J=9.0 Hz, 2H), 7.71 (d, J=8.1 Hz, 2H), 7.64 (d, J=8.7HZ, 2H), 7.49–7.39 (m, 6H), 7.36–7.27 (m, 2H), 7.24 (d, J=10.0 Hz, 2H), 7.16 (dd, J=9.7, 3.1 Hz, 1H), 7.13–7.06 (m, 4H), 6.68 (d, J=3.1 Hz, 2H), 6.23 (d, J=10.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=150.2, 150.1, 140.9, 137.4, 129.7, 129.6, 129.3, 128.6, 128.4, 127.0, 126.5, 126.2, 125.4, 125.3, 123.5, 121.2, 119.3, 118.2, 113.6, 80.4, 80.3, 21.2 ppm. IR (KBr): ν_{max}=3055, 3024, 2918, 1633, 1588, 1509, 1460, 1384, 1268, 1240, 1223, 1171, 1084, 1002, 942, 805, 745 cm^{-1}. HRMS (MALDI) calcd for $C_{44}H_{32}O_2S$: m/z (%): 647.2015 $[M+Na]^+$. Found: 647.2018 (61.3%).

*4.4.6. 2,5-Di-[3-(p-methoxyphenyl)-[3H]-naphtho[2,1-b]pyran-3-yl]-thiophene (**1f**).* The general procedure was followed and pale pink solid was obtained in yield of 72.8%. Mp 245.6–246.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.93 (d, J=8.4 Hz, 2H), 7.71 (d, J=8.1 Hz, 2H), 7.64 (d, J=9.0 Hz, 2H), 7.50–7.40 (m, 6H), 7.36–7.28 (m, 2H), 7.24 (d, J=10.0 Hz, 2H), 7.15 (dd, J=8.7, 2.2 Hz, 2H), 6.86–6.77 (m, 4H), 6.68 (d, J=3.1 Hz, 2H), 6.22 ppm (d, J=10.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=158.9, 150.3, 150.1, 135.9, 129.7, 129.6, 129.3, 128.4, 127.7, 127.0, 126.5, 125.3, 125.2, 123.5, 121.2, 119.3, 118.2, 113.6, 113.3, 80.2, 80.3, 55.2 ppm. IR (KBr): ν_{max}=3059, 3001, 2931, 2832, 1630, 16,089, 1587, 1508, 1459, 1382, 1305, 1248, 1230, 1174, 1082, 1034, 993, 948, 822, 812 cm^{-1}. HRMS (MALDI) calcd for $C_{44}H_{32}O_4S$: m/z (%): 679.1914 $[M+Na]^+$. Found: 679.1917 (30.4%).

*4.4.7. 2-[3-(p-Methoxyphenyl)-[3H]-naphtho[2,1-b]pyran-3-yl]-5-(3-phenyl-[3H]-naphtho[2,1-b]pyran-3-yl)-thiophene (**1g**).* The general procedure was followed and pale pink solid was obtained in yield of 65.1%. Mp 148–150 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.93 (d, J=8.1 Hz, 2H), 7.71 (d, J=8.1 Hz, 2H), 7.69–7.60 (m, 2H), 7.59–7.42 (m, 2H), 7.50–7.41 (m, 4H), 7.37–7.21 (m, 7H), 7.18 (dd, J=8.7, 2.4 Hz, 1H), 7.15 (dd, J=9.0, 3.1 Hz, 1H), 6.86–6.77 (m, 2H), 6.69 (d, J=3.1 Hz, 1H), 6.68 (d, J=2.5 Hz, 1H), 6.26 (d, J=10.0 Hz, 1H), 6.22 (d, J=9.7 Hz, 1H), 3.75 (s, 1.5H), 3.75 ppm (s, 1.5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.1, 150.6, 150.2, 150.2, 150.1, 144.0, 136.0, 129.9, 129.9, 129.7, 129.4, 128.5, 128.0, 127.8, 127.1, 127.0, 126.6, 126.3, 125.6, 125.5, 125.4, 125.3, 123.7, 123.6, 121.1, 119.6, 119.4, 118.3, 113.7, 113.3, 80.4, 80.4, 80.3, 80.2, 55.2 ppm. IR (KBr): ν_{max}=3058, 2923, 2834, 1633, 1606, 1587, 1509, 1460, 1385, 1302, 1249, 1227, 1205, 1173, 1085, 1003, 944, 812 cm^{-1}. HRMS (MALDI) calcd for $C_{43}H_{30}O_3S$: m/z (%): 649.1808 $[M+Na]^+$. Found: 649.1801 (31.4%).

*4.4.8. 2,5-Di-(2,6-diphenyl-5-ethoxycarbonyl-[2H]-naphtho[1,2-b]pyran-2-yl)-thiophene (**2a**).* The general procedure was followed and pale pink solid was obtained in yield of 87.6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.40 (dd, J=9.0, Hz, 2H), 7.64–7.55 (m, 4H), 7.54–7.46 (m, 4H), 7.46–7.24 (m, 18H), 6.80 (s, 2H), 6.77 (d, J=10.0 Hz, 2H), 6.22 (d, J=10.0 Hz, 2H), 3.97 (q, J=7.5 Hz, 4H), 0.86 ppm (t, J=7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.1, 150.3, 147.0, 143.9, 138.0, 132.7, 131.0, 130.4, 130.3, 128.5, 128.1, 127.8, 127.3, 127.1, 126.9, 126.7, 126.5, 126.1, 125.5, 125.4, 124.9, 122.1, 121.0, 111.7, 81.1, 61.1, 13.7 ppm. IR (KBr): ν_{max}=3057, 2977, 1728, 1639, 1501, 1446, 1370, 1292, 1225, 1174, 1108, 1039, 759, 699 cm^{-1}. HRMS (MALDI) calcd for $C_{60}H_{44}O_6S$: m/z (%): 915.2751 $[M+Na]^+$. Found: 915.2750 (95.6%).

*4.4.9. 2,5-Di-[2-(p-fluorophenyl)-6-phenyl-5-ethoxycarbonyl-[2H]-naphtho[1,2-b]pyran-2-yl]-thiophene (**2b**).* The general procedure was followed and red solid was obtained in yield of 81.9%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.39–8.32 (m, 2H), 7.60–7.46 (m, 8H), 7.46–7.28 (m, 12H), 7.06–6.95 (m, 4H), 6.80 (d, J=9.7 Hz, 1H), 6.80 (s, 2H), 6.79 (d, J=10.0 Hz, 1H), 6.18 (d, J=9.7 Hz, 1H), 6.17 (d, J=10.0 Hz, 1H), 3.97 (q, J=7.2 Hz, 2H), 3.96 (q, J=7.2 Hz, 2H), 0.86 (t, J=7.2 Hz, 3H), 0.86 ppm (J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.1, 162.1 (^1J=247.4 Hz), 150.2, 150.2, 146.8, 139.6, 137.9, 132.8, 131.3, 130.4, 130.3, 128.5, 128.1 (^3J=8.5 Hz), 127.9, 127.4, 127.1, 126.8, 126.6, 125.5, 125.4, 122.0, 122.0, 121.3, 115.0 (^2J=21.6 Hz), 111.7, 80.6, 80.6, 61.1, 13.7 ppm. IR (KBr): ν_{max}=2980, 1720, 1601, 1506, 1445, 1371, 1292, 1228, 1158, 1041, 933, 833, 770, 702 cm^{-1}. HRMS

(MALDI) calcd for $C_{60}H_{42}F_2O_6S$: *m*/*z* (%): 951.2562 $[M+Na]^+$. Found: 951.2552 (100%).

*4.4.10. 2,5-Di-[2-(o-fluorophenyl)-6-phenyl-5-ethoxycarbonyl-[2H]-naphtho[1,2-b]pyran-2-yl]-thiophene (**2c**).* The general procedure was followed and red solid was obtained in yield of 69.6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.85–7.38 (m, 2H), 7.68 (tt, *J*=7.8, 1.2 Hz, 2H), 7.57–7.48 (m, 4H), 7.47–7.22 (m, 14H), 7.08 (td, *J*=7.8, 1.2 Hz, 2H), 7.06 (dd, *J*=8.1, 0.9 Hz, 1H), 7.02 (dd, *J*=8.1, 0.9 Hz, 1H), 6.86 (d, *J*=1.2 Hz, 2H), 6.76 (d, *J*=10.0 Hz, 2H), 6.44 (d, *J*=10.0 Hz, 1H), 6.43 (d, *J*=10.0 Hz, 1H), 3.97 (q, *J*=7.2 Hz, 2H), 3.96 (q, *J*=7.2 Hz, 2H), 0.86 (t, *J*=7.2 Hz, 3H), 0.86 ppm (*J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.2, 153.4 (^1J=246.6 Hz), 153.3 (^1J=246.6 Hz), 149.1, 149.1, 146.7, 138.1, 132.9, 131.4, 130.5 (^2J=11.1 Hz), 130.5, 130.4, 129.9 (^3J=7.9 Hz), 128.6, 127.9, 127.4, 127.3, 127.1, 126.9, 126.7, 125.8, 125.8, 125.2, 125.1, 124.8, 123.9 (^4J=3.1 Hz), 122.1, 121.1, 116.5 (^2J=22.0 Hz), 111.6, 111.6, 79.3, 79.3, 79.2, 61.1, 13.5 ppm. IR (KBr): ν_{max}=3059, 2978, 1721, 1638, 1611, 1583, 1504, 1484, 1446, 1370, 1292, 1226, 1169, 1041, 758 cm^{-1}. HRMS (MALDI) calcd for $C_{60}H_{42}F_2O_6S$: *m*/*z* (%): 951.2562 $[M+Na]^+$. Found: 951.2544 (100%).

*4.4.11. 2-[2-(o-Fluorophenyl)-6-phenyl-5-ethoxycarbonyl-[2H]-naphtho[1,2-b]pyran-2-yl]-5-(2-(p-fluorophenyl)-6-phenyl-5-ethoxycarbonyl-[2H]-naphtho[1,2-b]pyran-2-yl)-thiophene (**2d**).* The general procedure was followed and red solid was obtained in yield of 87.4%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.46–8.33 (m, 2H), 7.73 (td, *J*=7.8, 1.1 Hz, 1H), 7.64–7.24 (m, 19H), 7.16–6.95 (m, 4H), 6.89 (d, *J*=3.7 Hz, 1H), 6.86–6.75 (m, 3H), 6.47 (dd, *J*=10.0, 1.9 Hz, 0.5H), 6.45 (dd, *J*=10.0, 1.9 Hz, 0.5H), 6.21 (d, *J*=10.0 Hz, 0.5H), 6.20 (d, *J*=10.0 Hz, 0.5H), 3.99 (q, *J*=7.2 Hz, 2H), 3.97 (q, *J*=7.2 Hz, 2H), 0.88 (t, *J*=7.2 Hz, 3H), 0.87 ppm (*J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.1, 168.0, 162.2 (^1J=246.6 Hz), 159.1 (^1J=248.7 Hz), 159.0 (^1J=248.7 Hz), 150.1, 150.0, 149.2, 149.1, 146.8, 146.6, 139.6 (^4J=2.8 Hz), 137.9, 137.9, 132.8, 131.3 (^2J=7.6 Hz), 130.5, 130.4, 130.3, 129.8 (^3J=7.9 Hz), 128.5, 128.2 (^3J=7.9 Hz), 128.2 (^3J=7.9 Hz), 127.8, 127.3, 127.1, 127.0, 126.8, 126.8, 126.7, 126.6, 125.6, 125.6, 125.5, 125.4, 125.2, 125.1, 124.8, 124.7, 123.9 (^4J=2.6 Hz), 122.0, 121.1, 116.5 (^2J=21.6 Hz), 116.5 (^2J=21.6 Hz), 115.0 (^2J=21.5 Hz), 111.6, 111.6, 111.6, 80.7, 80.7, 79.1, 61.1, 13.7 ppm. IR (KBr): ν_{max}=3058, 2956, 2927, 1720, 1636, 1601, 1505, 1370, 1226, 1158, 1040, 996, 815, 758 cm^{-1}. HRMS (MALDI) calcd for $C_{60}H_{42}F_2O_6S$: *m*/*z* (%): 951.2562 $[M+Na]^+$. Found: 951.2551 (100%).

*4.4.12. 2,5-Di-[2-(p-methylphenyl)-6-phenyl-5-ethoxycarbonyl-[2H]-naphtho[1,2-b]pyran-2-yl]-thiophene (**2e**).* The general procedure was followed and red solid was obtained in yield of 86.7%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.41 (d, *J*=7.8 Hz, 2H), 7.56–7.28 (m, 20H), 7.14 (dd, *J*=8.1, 3.7 Hz, 4H), 6.81 (d, *J*=1.2 Hz, 2H), 6.79 (d, *J*=10.0 Hz, 1H), 6.78 (d, *J*=10.0 Hz, 1H), 6.24 (d, *J*=10.0 Hz, 1H), 6.22 (d, *J*=10.0 Hz, 1H), 3.99 (q, *J*=7.2 Hz, 2H), 3.98 (q, *J*=7.2 Hz, 2H), 2.22 (s, 6H), 0.88 (t, *J*=7.2 Hz, 3H), 0.88 ppm (*J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.2, 150.4, 150.3, 147.0, 141.0, 140.9, 138.0, 137.8, 132.7, 130.9, 130.4, 130.3, 128.7, 128.5, 127.8, 127.3, 127.3, 126.9, 126.8, 126.7, 126.4, 126.1, 125.3, 125.2, 124.9, 122.2, 120.8, 111.7, 111.7, 81.0, 81.0, 61.0, 21.2, 13.7 ppm. IR (KBr): ν_{max}=2921, 1719, 1636, 1610, 1504, 1444, 1370, 1291, 1225, 1166, 1040, 931, 811, 769, 701 cm^{-1}. HRMS (MALDI) calcd for $C_{62}H_{48}O_6S$: *m*/*z* (%): 943.3064 $[M+Na]^+$. Found: 943.3053 (100%).

*4.4.13. 2,5-Di-[2-(p-methoxyphenyl)-6-phenyl-5-ethoxycarbonyl-[2H]-naphtho[1,2-b]pyran-2-yl]-thiophene (**2f**).* The general procedure was followed and red solid was obtained in yield of 79.8%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.41–8.34 (m, 2H), 7.56–7.27 (m, 20H), 6.87–6.80 (m, 4H), 6.85 (d, *J*=1.9 Hz, 2H), 6.77 (d, *J*=10.0 Hz, 1H), 6.76 (d, *J*=10.0 Hz, 1H), 6.20 (d, *J*=10.0 Hz, 1H), 6.19 (d, *J*=10.0 Hz, 1H), 3.97 (q, *J*=7.2 Hz, 2H), 3.96 (q, *J*=7.2 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 0.86 (t, *J*=7.2 Hz, 3H), 0.86 ppm (*J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.4, 159.2, 150.7, 150.6, 147.1, 138.2, 136.1, 136.1, 132.8, 131.1, 130.5, 130.5, 128.7, 128.7, 127.9, 127.7, 127.5, 127.4, 127.0, 126.8, 126.5, 125.4, 125.3, 122.3, 120.9, 113.7, 113.5, 111.8, 81.0, 80.9, 61.0, 22.6, 13.6 ppm. IR (KBr): ν_{max}=2930, 2835, 1720, 1608, 1509, 1463, 1443, 1371, 1292, 1253, 1226, 1175, 1040, 827, 770, 702 cm^{-1}. HRMS (MALDI) calcd for $C_{62}H_{48}O_8S$: *m*/*z* (%): 975.2962 $[M+Na]^+$. Found: 975.2952 (70.5%).

*4.4.14. 2-[2-(2,6-Diphenyl)-5-ethoxycarbonyl-[2H]-(naphtho[1,2-b]pyran-2-yl)-5-[2-(p-methoxyphenyl)-5-ethoxycarbonyl-6-phenyl-[2H]-(naphtho[1,2-b]pyran-2-yl)-thiophene (**2g**).* The general procedure was followed and red solid was obtained in yield of 82.7%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.45–8.34 (m, 2H), 7.65–7.57 (m, 2H), 7.56–7.28 (m, 19H), 6.88–6.74 (m, 8H), 6.25 (d, *J*=10.0 Hz, 0.5H), 6.24 (d, *J*=10.0 Hz, 0.5H), 6.21 (d, *J*=10.0 Hz, 0.5H), 6.20 (d, *J*=10.0 Hz, 0.5H), 3.99 (q, *J*=7.2 Hz, 2H), 3.98 (q, *J*=7.2 Hz, 2H), 3.77 (s, 3H), 0.88 (t, *J*=7.2 Hz, 3H), 0.87 ppm (*J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.2, 159.0, 150.7, 150.6, 150.2, 150.1, 147.0, 147.0, 143.9, 143.9, 138.0, 135.9, 135.9, 132.7, 132.7, 131.0, 130.9, 130.4, 130.3, 128.6, 128.1, 127.8, 127.6, 127.6, 127.3, 127.2, 126.9, 126.9, 126.7, 126.5, 126.4, 126.1, 125.5, 125.4, 125.2, 125.1, 124.9, 122.1, 120.9, 120.8, 113.4, 111.7, 81.1, 81.0, 80.9, 80.9, 61.1, 22.7, 13.7 ppm. IR (KBr): ν_{max}=3057, 2954, 2927, 1719, 1636, 1607, 1508, 1444, 1370, 1291, 1254, 1225, 1174, 1144, 1109, 1040, 931, 810, 770, 700 cm^{-1}. HRMS (MALDI) calcd for $C_{61}H_{46}O_7S$: *m*/*z* (%): 945.2857 $[M+Na]^+$. Found: 945.2864 (100%).

Supplementary data

Synthesis of intermediates. Isolation of the colored forms, measurement on kinetics of photocoloration and thermal fading, as well as fatigue-resistance of photochromic compounds. Copies of NMR spectra. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.04.068. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Durr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, The Netherlands, 1990; (b) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum: New York, NY, 1999; (c) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001; (d) Irie, M. *Chem. Rev.* **2000**, *100*, 1685; (e) Tian, H. *Chem. Commun.* **2007**, 781; (f) Russew, M. M.; Hecht, S. *Adv. Mater.* **2010**, *22*, 3282.
2. For a review, see: Raymo, F. M.; Tomasulo, M. *J. Phys. Chem. A* **2005**, *109*, 7343.
3. For diarylethene, see: (a) Areephong, J.; Logtenberg, H.; Browne, W. R.; Feringa, B. L. *Org. Lett.* **2010**, *12*, 2132; (b) Areephong, J.; Hurenkamp, J. H.; Milder, M. T. W.; Meetsma, A.; Herek, J. L.; Browne, W. R.; Feringa, B. L. *Org. Lett.* **2009**, *11*, 721; (c) Higashiguchi, K.; Matsuda, K.; Tanifuj, N.; Irie, M. *J. Am. Chem. Soc.* **2005**, *127*, 8922; (d) Higashiguchi, K.; Matsuda, K.; Irie, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3537; (e) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2001**, *123*, 9896; (f) Luo, Q.; Chen, B.; Wang, M.; Tian, H. *Adv. Funct. Mater.* **2003**, *13*, 233; (g) Kaieda, T.; Kobatake, S.; Miyasaka, H.; Murakami, M.; Iwai, N.; Nagata, Y.; Itaya, A.; Irie, M. *J. Am. Chem. Soc.* **2002**, *124*, 2015.
4. For benzodihydropyrene, see: (a) Mitchell, R. H.; Ward, T. R.; Chen, Y.; Wang, Y.; Weerawarna, S. A.; Dibble, P. W.; Marsellam, M. J.; Almutair, A.; Wang, Z. *J. Am. Chem. Soc.* **2003**, *125*, 2974; (b) Mitchell, R. H.; Ward, T. R.; Wang, Y.; Dibble, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 2601.
5. For spiropyran, see: (a) Shao, N.; Jin, J.-Y.; Wang, H.; Zheng, J.; Yang, R.-H.; Chan, W.-H.; Abliz, Z. *J. Am. Chem. Soc.* **2010**, *132*, 725; (b) Zhang, Q.; Ning, Z.; Yan, Y.; Qian, S.; Tian, H. *Macromol. Rapid Commun.* **2008**, *29*, 193; (c) Wen, G.; Yan, J.; Zhou, Y.; Zhang, D.; Mao, L.; Zhu, D. *Chem. Commun.* **2006**, 3016.
6. For spirooxazine, see: Kumar, S.; Watkins, D. L.; Fujiwara, T. *Chem. Commun.* **2009**, 4369.
7. For diarylpyran, see: (a) Kickova, A.; Donovalova, J.; Kasak, P.; Putala, M. *New J. Chem.* **2010**, *34*, 1109; (b) Gabbutt, C. D.; Heron, B. M.; Instone, A. C.; Kolla, S. B.; Mahajan, K.; Coelho, P. J.; Carvalho, L. M. *Dyes Pigments* **2008**, *76*, 24; (c) Moorthy, J. N.; Venkatakrishnan, P.; Samanta, S. *Org. Biomol. Chem.* **2007**, *5*, 1354; (d) Samat, A.; Lokshin, V.; Chamontin, K.; Levi, D.; Pepe, G.; Guglielmetti, R. *Tetrahedron* **2001**, *57*, 7349.
8. (a) Zhao, W.; Carreira, E. M. *J. Am. Chem. Soc.* **2002**, *124*, 1582; (b) Zhao, W.; Carreira, E. M. *Chem.—Eur. J.* **2007**, *13*, 2671; (c) Zhao, W.; Carreira, E. M. *Org. Lett.* **2006**, *8*, 99.
9. For hybrid systems, see: (a) Delbaere, S.; Vermeersch, G.; Frigoli, M.; Mehl, G. H. *Org. Lett.* **2010**, *12*, 4090; (b) Delbaere, S.; Micheau, J.-C.; Frigoli, M.; Mehl, G. H.;

Vermeersch, G. *J. Phys. Org. Chem.* **2007**, *20*, 929; (c) Delbaere, S.; Vermeersch, G.; Frigoli, M.; Mehl, G. H. *Org. Lett.* **2006**, *8*, 4931; (d) Frigoli, M.; Mehl, G. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 5048.
10. The reported procedure only afforded low yield of diacylthiophene see: (a) Hartough, H. D.; Kosak, A. I. *J. Am. Chem. Soc.* **1947**, *69*, 1012; (b) Hartough, H. D.; Kosak, A. I. *J. Am. Chem. Soc.* **1947**, *69*, 3098.
11. Zhao, W.; Carreira, E. M. *Org. Lett.* **2003**, *5*, 4153.
12. Gemert, B. V. Benzo and Naphthopyrans (Chromenes) In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum: New York, NY, 1999.
13. Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636.
14. (a) Delbaere, S.; Buccioni-Houze, B.; Bochu, C.; Teral, Y.; Campredon, M.; Vermeersch, G. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1153; (b) Delbaere, S.; Micheau, J. C.; Vermeersch, G. *J. Org. Chem.* **2003**, *68*, 8968.
15. Murov, S. L.; Carmichael, L.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, NY, 1993; pp 298–305.
16. Becker, R. S.; Pelliccioli, A. P.; Romani, A.; Favaro, G. *J. Am. Chem. Soc.* **1999**, *121*, 2104.