Dyes and Pigments 119 (2015) 95–107

Contents lists available at ScienceDirect

Dyes and Pigments

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

Substituent effects on the photochromic properties of 3,3-diphenyspiro[benzofluorenopyran-cyclopentaphenanthrene]s

Junji Momoda [a, b, **], Shinobu Izumi [c], Yasushi Yokoyama [b, *]

[a] Fine Chemical Sales Department, Tokuyama Corp. Ltd., Kasumigaseki Common-Gate West, 3-2-1, Kasumigaseki, Chiyoda, Tokyo, 100-8983, Japan
[b] Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, 79-5, Tokiwadai, Hodogaya, Yokohama, 240-8501, Japan
[c] Analysis Team, Quality Assurance Group, SUN-TOX Co. Ltd., 1-1, Harumicho, Shunan, 745-0024, Japan

ARTICLE INFO

Article history:
Received 13 February 2015
Received in revised form
15 March 2015
Accepted 17 March 2015
Available online 25 March 2015

Keywords:
Photochromism
Naphthopyran
Ophthalmic lenses
Phenanthrene
Substituent effect
Fading rate

ABSTRACT

The introduction of electron-donating groups on the skeleton of a naphthopyran, 3,3-diphenyspiro [benzofluorenopyran-cyclopentaphenanthrene], has led to the development of a photochromic dye applicable to photochromic lenses. Introducing a methoxy group to C6 moved the absorption band of the MC form towards the longer wavelength. Further introduction of methoxy groups to the para-position of the phenyl groups on C3 induced faster decoloration of the MC form. Additional introduction of a methoxy group to C13 led to the enhancement of the absorption intensity as well as the facile, economic synthesis of the dye caused by the symmetrical property of the starting material.

1. Introduction

Naphthopyrans have been shown to exhibit thermally reversible photochromism [1,2]. According to their substitution patterns, naphthopyrans are classified into two types: 2*H*-naphtho[1,2-*b*]pyran and 3*H*-naphtho[2,1-*b*]pyran, as shown in Scheme 1. Their photchromic reactions involve 6π-electrocyclizations between a pyran ring (NP form, usually colorless) and a 1-oxo-2,4-pentadiene skeleton (MC form, colored).

The photochromism of naphthopyrans was first reported by Becker in 1969 [3]. Their photochromism was, however, observed only at low temperatures and the fatigue resistivity was poor compared to that of spirooxazines. Therefore, spirooxazines were investigated more favorably from the viewpoint of commercial applications such as ophthalmic lenses.

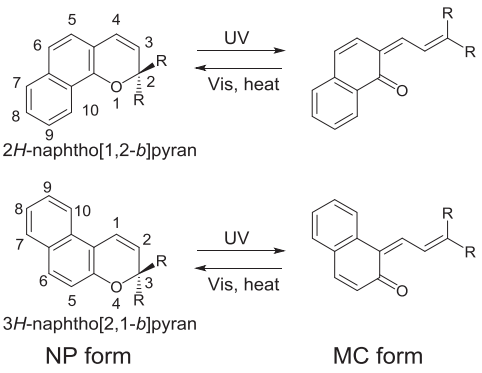
Until the beginning of the 1980 s, inorganic photochromic lenses such as PhotoGray Extra® developed by the Coring Corp. monopolized the market. In 1982, the American Optical Co. launched plastic photochromic lenses using spirooxazines under the name Photo Lite®. However, because it exhibited only a blue color upon UV irradiation, it was not widely used and neutral colors such as gray or brown were more favored. In addition, darkness of the coloring under sunlight was insufficient for use as sunglasses. Consequently, since the late 1980 s, naphthopyrans began to be more widely studied over spirooxazines, and gray and brown naphthopyrans had been developed by the mid-1990 s [4,5]. Meanwhile, several naphthopyrans were launched into the market by Tokuyama Corp. for use in photochromic auto-color-regulating ophthalmic lenses, and their properties have also been continuously improved. In fact, basic research [6–8] as well as the development of commercially applicable compounds [9] have been carried out extensively by a number of researchers and companies.

In order for a photochromic dye to be used for auto-color-regulating ophthalmic lenses, it should, by itself, satisfy the following conditions:

1) Completely colorless when in the closed form
2) Exhibits a neutral color, such as gray or brown, when in the colored open form
3) Coloring should be sufficiently dark when UV light is applied
4) The color should fade quickly when UV light is discontinued

* Corresponding author. Tel./fax: +81 45 339 3934.
** Corresponding author. Tel.: +81 3 3597 5105.
E-mail addresses: j-momoda@tokuyama.co.jp (J. Momoda), yyokoyam@ynu.ac.jp (Y. Yokoyama).

http://dx.doi.org/10.1016/j.dyepig.2015.03.019
0143-7208/



Scheme 1. Structure and photochromism of naphthopyrans.

5) The photochromic dyes should be highly fatigue resistant

To address these issues, we have long continued research on 2*H*-naphthopyrans with two phenyl groups on the C2 carbon atom. Recently, we have developed 3,13-dihydrobenzo [3,4] fluoreno [2,1-*b*]pyrans, which belong to the 2*H*-naphtho[1,2-*b*]pyran group for use in photochromic ophthalmic lenses [10–12]. In this article, we report on our recent research efforts to realize a dye that satisfies the above required conditions with the 3,13-dihydrobenzo [3,4] fluoreno[2,1-*b*] pyran skeleton [13].

2. Results and discussion

2.1. Acceleration of fading reaction

2.1.1. Stability of isomers and conformers for MC forms of prototype compounds estimated by DFT

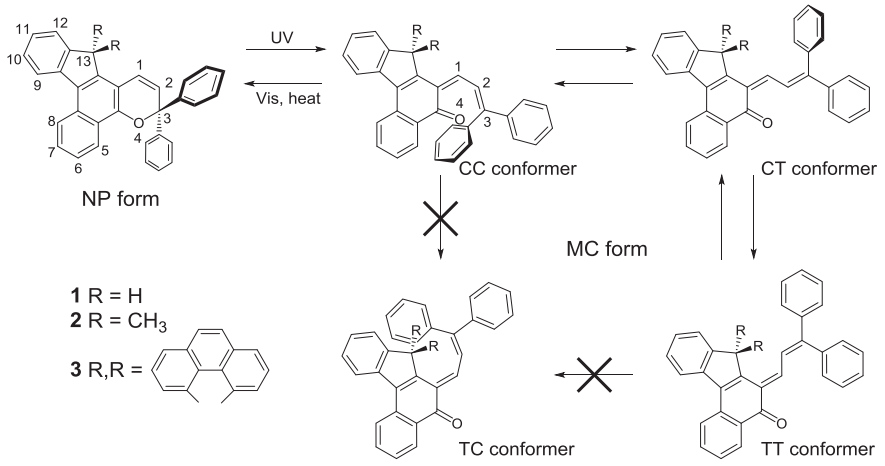
The photochromic reactions including the isomerization between the conformers of the MC form of 3,13-dihydrobenzo[3,4] fluoreno[2,1-*b*]pyrans are detailed in Scheme 2 [6].

Upon UV irradiation, the colorless NP form opens its pyran ring to afford a highly congested CC (*cis* – *s-cis*) conformer which may isomerize to yield other conformers by either a fast single bond rotation and/or double bond isomerization. Namely, by the rotation of the C1–C2 single bond, the CT (*cis* – *s-trans*) conformer is formed, which then isomerizes to the TT (*trans* – *s-trans*) conformer by E-Z isomerization of the exo-cyclic double bond on the cyclohexadienone ring. The TC (*trans* – *s-cis*) conformer could be generated either from the CC conformer by E-Z isomerization of the exo-cyclic double bond or from the TT conformer by rotation of the C1–C2 single bond. However, for compounds having a 3,13-dihydrobenzo [3,4] fluoreno[2,1-*b*]pyran skeleton, severe steric repulsion between one of the phenyl groups on C3 and the substituents on C13 causes the TC conformer to be considerably unstable. Therefore, we judged that mainly CT and TT conformers that can exist stably as the MC form of 3,13-dihydrobenzo [3,4] fluoreno [2,1-*b*]pyrans should be considered.

When the colored MC form thermally reverts back to the colorless NP form, the MC form should take the CC conformer as its immediate precursor. Since the CT conformer can isomerize to the CC conformer thermally by rotation of the C1–C2 single bond, the activation energy between the CT and CC conformers may be small. When the CT conformer is unstable, the fading rate quickens. On the other hand, the TT conformer should first convert to the CT conformer before it changes to the NP form by thermal E-Z isomerization of the exo-cyclic double bond, which usually has a higher activation energy than the single bond rotation. Thus, disappearance of the MC form takes longer when the TT conformer is stable and its proportion is large. In order to accelerate the fading rate, it would thus be effective to reduce the stability of both the CT and TT forms. In contrast, to strengthen coloration, it would be effective to increase the stability of the CT and TT forms since coloration becomes stronger when the fading reaction is slow.

DFT calculations [14] of the NP and MC forms of the prototype 3,13-dihydro-3,3-diphenylbenzo[3,4]fluoreno[2,1-*b*]pyran **1**, sterically congested 3,13-dihydro-13,13-dimethyl-3,3-diphenylbenzo [3002C4]fluoreno[2,1-*b*]pyran **2** and 3,3-diphenylspiro[benzo[3,4] fluoreno[2,1-*b*]pyran-13(3*H*),4'-[4*H*]cyclopenta[def]phenanthrene **3** showed that the CT and TT forms of **2** and **3** have considerably higher energy than **1**. This probably arises from the steric congestion between one of the phenyl groups on C3 and the substituents on C13, i.e., the geminal dimethyl group in **2** and the spirophenanthrene group in **3**. The calculation results are shown in Table 1, where the energy for the NP form of each compound was set at zero.

For the CC conformers, the energy values of all the compounds are much higher than their NP forms, as supposed from their sterically congested structures. The TC forms are also unstable due to their congested structures. For **3**, the TC conformer did not converge to a local minimum and showed a structure similar to its TT conformer having a local minimum energy. We, thus, needed to consider only the CT and TT conformers as the main conformers of the MC form.



Scheme 2. Photochromism of 3,13-dihydrobenzo[3,4]fluoreno[2,1-*b*]pyrans.

Table 1
DFT calculation results of the NP and MC forms of naphthopyrans[a].

	NP	CC	CT	TT	TC	TT/CT
1	0	47.25	1.86	9.35	44.59	0.048
2	0	54.98	7.75	31.19	72.98	0.00008
3	0	50.93	13.91	29.89	35.03[b]	0.0016

[a] Energy: kJ mol^{-1}.
[b] The structure is similar to TT.

Introduction of substituents on C13 of **1** increased the instability of both the TT and CT forms. However, since the phenanthrene ring in **3** is flat and located perpendicular to the naphthalene ring, the steric hindrance which may be exerted is not much larger than that of **2**. Therefore, the activation energy value for the thermal isomerization of the exo-cyclic double bond between **2** TT and **2**CT is comparable to that between **3** TT and **3**CT. In addition, since the isomerization from CT to CC occurs without causing any steric repulsion between the substituents on C13 and phenyl group on C3, the activation energy for thermal isomerization of the C1–C2 single bond rotation for **2**CT and **3**CT can also be regarded as comparable. Furthermore, since the up-hill energy difference from CT to CC is decisively larger for **2** when compared to **3** by 10 kJ mol^{-1}, the thermal reaction from **3**CT to **3**CC may be much faster than that from **2**CT to **2**CC.

Results of DFT calculations showed that introduction of the phenanthrene group as a spiro-structure, as shown in **3**, would bring about: (1) a more stable CC conformer than **2** with the geminal dimethyl group, (2) a less stable CT conformer than **2**, and (3) an unstable TT conformer similar to **2**. As a whole, although the precise activation energies between the conformers were not examined, we theorized that thermal decoloration of the MC form of **3** would occur faster than that of **2**. These expectations prompted us to synthesize **3**, together with other related derivatives with different substituents on **3** in order to improve its photochromic properties for effective use in photochromic ophthalmic lenses.

2.1.2. Synthesis of the compounds

Naphthopyran **3** and other related compounds, which will be discussed later, were synthesized, as shown in Scheme 3.

The key intermediates for the synthesis of naphthopyrans used in this study were **12**, i.e., keto-nephthols with various substitution patterns. Synthesis of **12** was initiated by Stobbe condensation of benzophenone with diethyl succinate followed by the two-step Friedel–Crafts type cyclization of two carboxylic acid moieties with their nearest aromatic rings. The reaction procedures have been reported in the previous literature [15].

Syntheses of naphthopyrans **3**, **4**, **6** and **7** used in this study were carried out by the construction of a naphthopyran moiety from **12**, followed by the formation of a spirophenanthrene moiety with the addition of 4-lithiophenanthrene to **13** and acid catalyzed dehydrative ring closure. On the other hand, naphthopyrans **5** and **8** were obtained by first forming the spirophenanthrene moiety and then constructing the naphthopyran skeleton.

2.1.3. Photochromism and fading reaction rate of *3*

The absorption spectra of the NP form and the photostationary state (pss) for the UV irradiation of **2** and **3** in toluene are shown in Fig. 1. The fading rate of the colored form of **3** was examined first. After UV light irradiation to each toluene solution of **2** and **3** (5.8×10^{-3} mol dm^{-3}) at 23 °C until it reached the pss, the change in absorbance at the absorption maximum wavelength was monitored (Fig. 2). As expected from analysis of DFT calculations, spirophenanthrene-naphthopyran **3** showed a faster fading rate than gem-dimethyl-naphthopyran **2**, as shown in Table 2. Thus, the introduction of the spiro-phenanthrene group proved to be effective in accelerating the color fading rate.

However, two drawbacks were found for **3**. First, its color in the MC form was violet, which is not preferable for practical use in ophthalmic lenses. In addition, the fading rate was still rather slow.

2.2. Improvement of absorption spectral character of *3*

The preferable colors for ophthalmic lenses are either gray or brown, which can be accomplished when absorption covers the entire visible region with uniform intensity. Since naphthopyran **3** has two absorption bands in the visible region, it requires a bathochromic shift of the larger absorption band in the longer wavelength region and enlargement of the absorption intensity of the second absorption band in the shorter wavelength region. Some perturbation on the electronic character of the conjugation system of the MC form seemed to be the most effective way to realize these modifications. Since the carbonyl group in the MC form is electron-withdrawing, we first examined the effects of introducing an electron-donating group into the molecule.

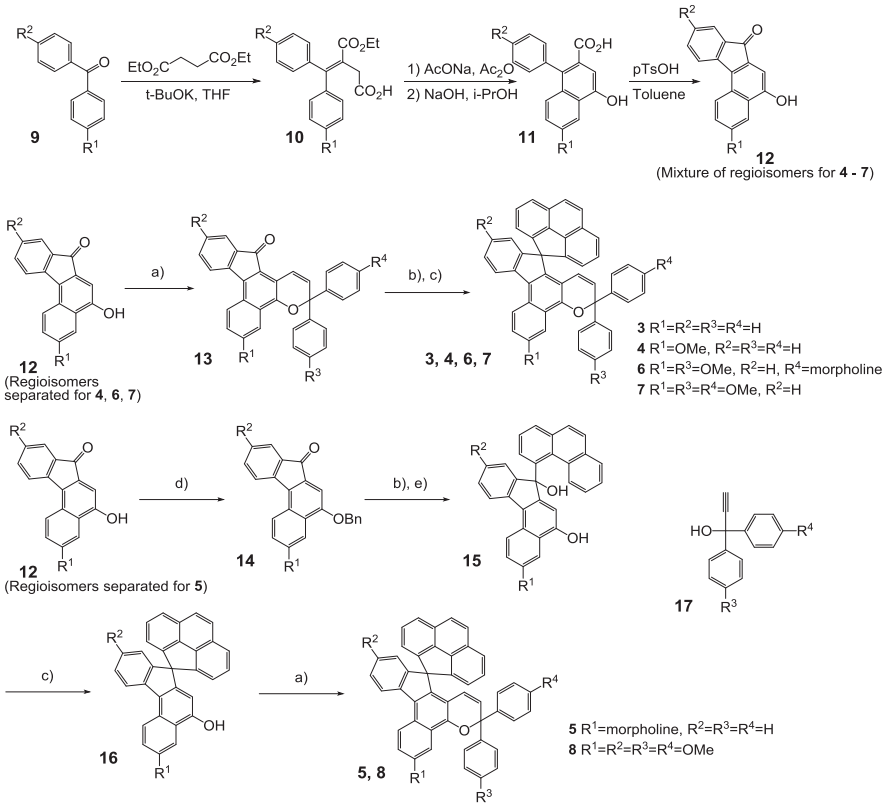
2.2.1. Substituent effects on the absorption spectra of acetophenones

Acetophenone was selected as the model compound for the partial structure of the MC form and the effects of the substitution position for the methoxy group on the absorption spectra were investigated. The spectra and the structure of the compounds are shown in Fig. 3 and the absorption spectral properties are summarized in Table 3.

When the methoxy group was substituted on the para position (**21**) which conjugates with the carbonyl group of acetophenone **18**, the total shape of its absorption spectrum largely changed. Although the absorption maximum wavelength of the longest $\pi\pi^*$ transition did not change, the molar absorption coefficient of **21** became fifteen times larger than that of **18**. On the other hand, when the methoxy group was substituted either on the ortho position (**19**), with severe steric hindrance to avoid maintaining coplanarity of the acetyl group with the aromatic ring, or meta position (**20**) which is out of conjugation with the carbonyl group, the longest $\pi\pi^*$ absorption maxima of both isomers showed bathochromic shifts of *ca.* 40 nm. A similar phenomenon was observed for indolylfulgides [16]. When this idea is applied to our naphthopyran system, the introduction of a methoxy group on C5 (ortho), C6 or C8 (meta) seemed to be effective in inducing a bathochromic shift of the absorption band in the longer wavelength region. From the viewpoint of developing facile synthetic pathways, we decided to introduce an electron-donating group to C6, one of the meta positions to the carbonyl group of the MC form.

2.2.2. Substituent effects on C6 for the absorption spectra of the MC form examined by DFT calculations

The substituent effects on C6 with different electron-donating powers were examined by DFT calculations. The absorption spectra of the CT conformers of the MC forms of **3**, **4**, and **5** obtained are shown in Fig. 4. It is apparent that the introduction of an electron-donating group on C6 of **3 MC** is effective in inducing a bathochromic shift, and the shift is larger when the electron-donating ability is larger. Therefore, the C6-morpholine-substituted **5** seemed to be superior to C6-methoxy-substituted **4**. However, one concern was the large cleft at 500 nm in the calculated spectra of **5**. Since the coverage of the visible light region between 400 and 600 nm is better for **4**, we decided to prepare both compounds and compare their spectroscopic characters.



Scheme 3. General synthetic route of the naphthopyrans used in this study.

2.2.3. Photochromism of **4** and **5**

Photochromic reactions of C6-substituted naphthopyrans were carried out in toluene at 23 °C. The spectroscopic and photochromic properties of C6-methoxy-substituted **4** and C6-morpholine-substituted **5** are summarized in Table 4 together with those of **3**. The absorption spectra of the MC forms of **3**, **4** and **5** are depicted in Fig. 5.

In proportion to the largeness of the electron-donating ability of the substituent at C6, the absorption band of **3** at around 420 nm became larger and the absorption band at around 520 nm shifted substantially towards longer wavelengths. Eventually, **5** showed a brownish color after UV irradiation. However, the fading rate of the MC form of **5** became slower than that of **3** (Fig. 6).

The reason why the fading rate decreased when the electron-donating group was introduced on C6 can be interpreted as follows: When the resonance structures of the CT conformers of **4** and **5** in which the lone pair on the oxygen or nitrogen atom on C6 participates is considered, the C1–C2 single bond in **3** acts as a double bond (Scheme 4). It would cause slower isomerization from CT to CC conformers by thermal reaction. Therefore, we needed to increase the fading rate with further structural as well as electronic modification of the molecule since the colorings for the MC form of **4** and **5** were almost acceptable.

2.2.4. Absorption spectral properties of the NP forms of **3**, **4** and **5**

Before carrying out further molecular modifications, the color of the NP form was examined. The absorption spectra of the NP forms of **3**, **4** and **5** were measured in toluene of 5×10^{-4} mol dm^{-3} concentration (Fig. 7).

In order to use naphthopyran for ophthalmic lenses, its thermally stable form needs to be colorless. The absorption spectra of **5** showed that its NP form has a yellow hue, while **3** and **4** are almost colorless.

Because of these two drawbacks for **5** (slow fading of the MC form and a strong yellow hue of the NP form), we selected **4** to apply further structural modifications.

2.3. Introduction of electron-donating groups on the C4′ positions of the two phenyl groups on C3 of **4**

Since the introduction of a methoxy group on C6 caused a retardation of the color fading rate in its MC form by increasing the double bond character of the C1–C2 bond, we then tried introducing an electron resonance character which occurs towards the opposite direction to that generated by the methoxy group on C6. Namely, we introduced electron-donating groups on the C4′ positions of the phenyl groups on C3 [2]. The C4′ position on a C3 phenyl group is located at the other end of the long conjugation system with the methoxy group on C6. Therefore, the newly introduced electron donating group may weaken the electron-donating ability of the methoxy group on C6 to the conjugation system so that the double bond character of C1–C2 bond may decrease. However, the electron-donating function from the meta position of the carbonyl group could be maintained. The basic principle is shown in Scheme 5.

Accordingly, we synthesized **6** with one methoxy group on C4′ and one morpholine group on C4′ of the other phenyl group as well as **7** with two methoxy groups on both C4′ positions of the phenyl groups on C3. Their syntheses were carried out similarly to the procedures for other naphthopyrans, as shown in Scheme 3.

2.3.1. Photochromism of **6** and **7**

The effect of the electron-donating groups on the C3 phenyl groups on the fading rate was remarkable. That is, the fading rate of the MC form could be greatly accelerated. In addition, the two absorption bands in the visible region moved to longer

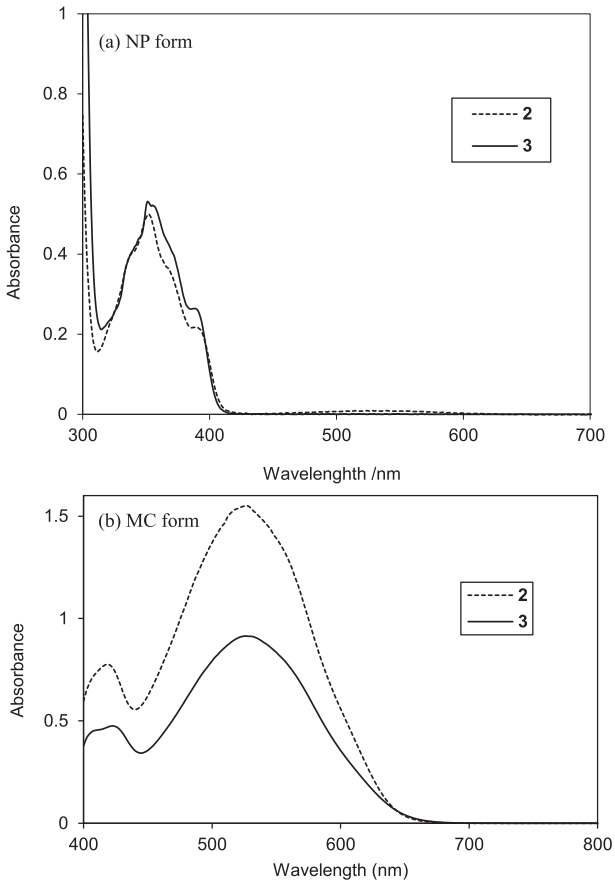


Fig. 1. Absorption spectra of naphthopyrans **2** and **3** in toluene at 23 °C. (a) NP forms; (b) MC forms. Concentration: (a) 5.0×10^{-5} mol dm^{-3} for NP form. (b) 5.8×10^{-3} mol dm^{-3} for MC form Irradiation condition for (b): Xenon lamp (300 nm - 500 nm based on ISO regulation).

wavelengths by 20–50 nm. Data for the absorption spectral properties and fading rate of the MC forms of **4**, **6**, and **7** are summarized in Table 5, and the absorption spectra of **6** and **7** at the photostationary state are shown in Fig. 8.

One drawback for **6** and **7** is the smaller absorbance of their MC forms under the same irradiation conditions at the same reaction temperature as **4** which was caused by fast thermal fading. Although this problem may be solved by introducing the

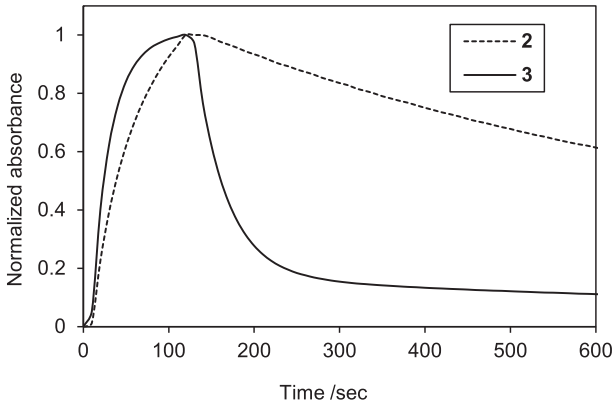


Fig. 2. Photocoloration and thermal fading of **2** and **3** in toluene at 23 °C. Solvent and concentration: Toluene (5.8×10^{-3} mol dm^{-3}). Irradiation: Xenon lamp (300 nm - 500 nm based on ISO regulation). Detection wavelength: **2**: 525 nm; **3**: 527 nm.

Table 2
Photochromic properties of **2** and **3** in toluene at 23 °C.

Naphthopyrans	λ_{max}/nm	Absorbance of MC form at pss	Fading rate	
			$t_{1/2}$/sec[a]	$t_{3/4}$/sec[a]
2	418	0.80	629	–
	525	1.60	660	–
3	423	0.47	31	74
	527	0.91	33	81

[a] $t_{1/2}$: Half life time. $t_{3/4}$: Time required for three quarters of the initial absorbance disappears.

naphthopyran dye into polymer matrices where the fading rate becomes slower than that in solution [17], further improvement of the spectral properties to increase their molar absorption coefficients is desired.

Another drawback was observed for **6**. When the solutions of **4**, **6**, and **7** after the photoreaction were placed in the dark, only the solution for **6** showed a purple hue which was unsuitable as material for ophthalmic lenses. Although the absorption maximum wavelength in the longer wavelength of **6** just after UV irradiation was 589 nm, as shown in Fig. 8, the absorption maximum of the remaining band in Fig. 9 was 580 nm. Therefore, we assumed that the major MC form showing the absorption band in Fig. 8 was the CT form since it disappeared quickly, and the remaining MC form showing a small absorption band in Fig. 9 was the TT form. Because the strong electron-donating ability of the nitrogen atom on the phenyl ring caused the strong conjugation, the isomerization rate from the TT to CT form was retarded. Consequently, we chose **7** as the candidate for a fast fading photochromic dye applicable to ophthalmic lenses. However, it still showed weak coloration upon UV irradiation due to fast fading. If the molar absorption coefficient of the absorption band of **7** in the visible region could be increased, it would be the perfect dye.

2.4. Final improvement of absorption spectral characters of 7

2.4.1. Molecular design

The coloration of **7** was weaker than **4** due to its faster decoloration caused by a decrease in the double bond character of the

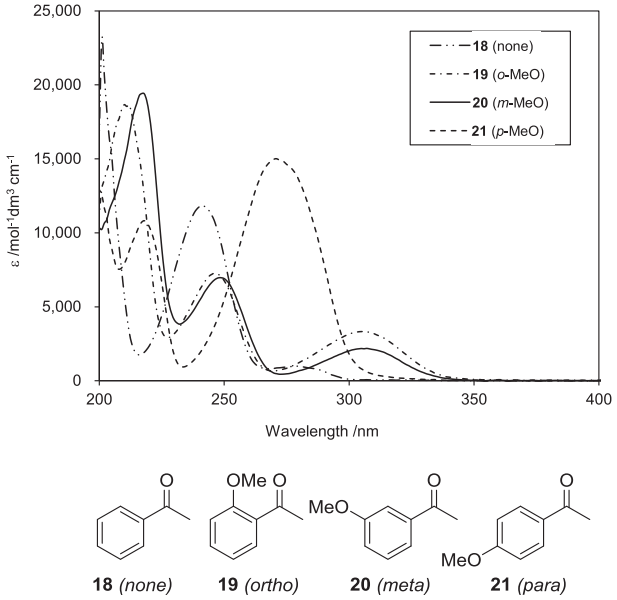


Fig. 3. UV spectra of methoxy-substituted acetophenones **18** (none), **19** (orhto), **20** (meta), and **21** (para). Solvent: Methanol. Concentration: 1.2×10^{-4} mol dm^{-3}.

Table 3
Absorption spectral data of acetophenone derivatives.

Substituent	λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})	
18 (none)	241(11,900)	279(1000)
19 (*o*-methoxy)	246(7300)	306(3300)
20 (*m*-methoxy)	248(7000)	305(2200)
21 (*p*-methoxy)	218(10,800)	278(15,000)

Solvent: Methanol.
Concentration: 1.2 × 10^{-4} mol dm^{-3}.

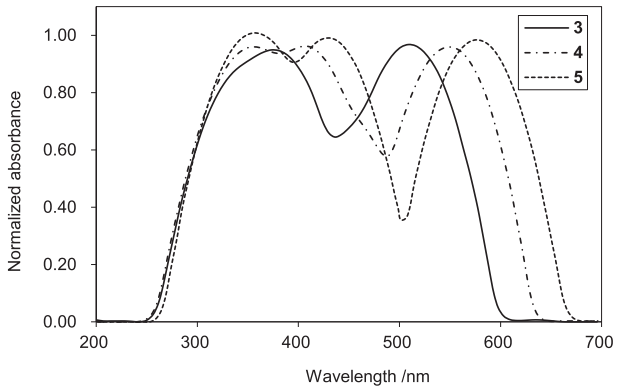


Fig. 4. UV–Vis spectra of CT conformer of MC-form of C6-substituted naphthopyrans obtained by DFT calculations.

C1–C2 bond. In order to reduce the electron donating ability of the methoxy groups on the two C4′ positions of the phenyl group on C3, two ways can be considered. One is to remove one of the methoxy groups on the C3 phenyl groups. The other is to introduce another

Table 4
Spectral data and fading rate data of **4** and **5** in toluene at 23 °C.

Naphthopyran	λ_{max}/nm	Absorbance of MC form	Fading rate	
			$t_{1/2}$/sec[a]	$t_{3/4}$/sec[a]
3	423	0.47	31	74
	527	0.91	33	81
4	416	0.59	51	136
	549	0.87	57	197
5	430	1.00	109	589
	573	0.96	138	1040

[a] $t_{1/2}$: Half life time. $t_{3/4}$: Time required for three quarters of the initial absorbance disappears.

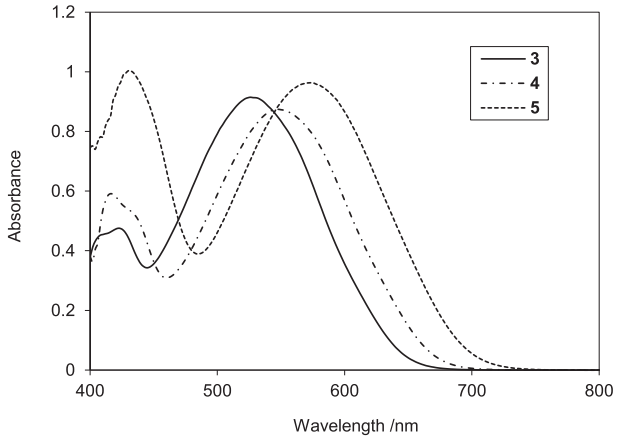


Fig. 5. Absorption spectra of MC form of **3**, **4** and **5** in toluene at 23 °C. Solvent and concentration: Toluene (5.8 × 10^{-3} mol dm^{-3}). Irradiation: Xenon lamp (300 nm – 500 nm based on ISO regulation).

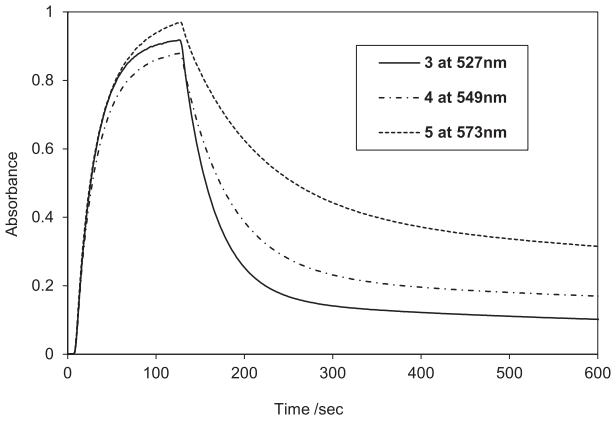
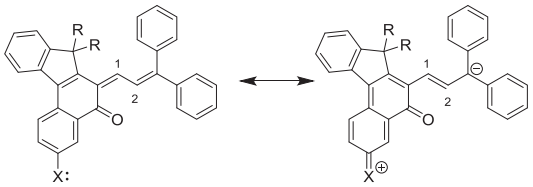


Fig. 6. Photocoloration and thermal fading of **3**, **4**, and **5** in toluene at 23 °C. Solvent and concentration: Toluene (5.8 × 10^{-3} mol dm^{-3}). Irradiation: Xenon lamp (300 nm – 500 nm based on ISO regulation). Detection wavelength: **3**: 527 nm; **4**: 549 nm; **5**: 573 nm.



Scheme 4. Effect of an electron-donating group on C6 of **4** and **5** on the resonance structure.

electron-donating group on the molecule to reduce the electron-donating ability of the methoxy groups on the C3 phenyl groups by competing with the direction of electron movement in resonance structure formation. As shown in Scheme 6, if a methoxy group is introduced on C11 of the indene moiety, it will have a resonance structure with a similar effect on the C1–C2 bond character as the methoxy group on C6. This strategy was adopted since there is a big advantage for synthesis of this molecule.

Since the starting material for the synthesis of **12**, i.e., the synthetic key intermediate of **8** in Scheme 3, was benzophenone **9**, introduction of two methoxy groups on C6 and C11 in **8** led to the introduction of a symmetric factor to **9**, i.e., 4,4′-bismethoxybenzophenone. In order to synthesize naphthopyrans **4**, **6** and **7**,

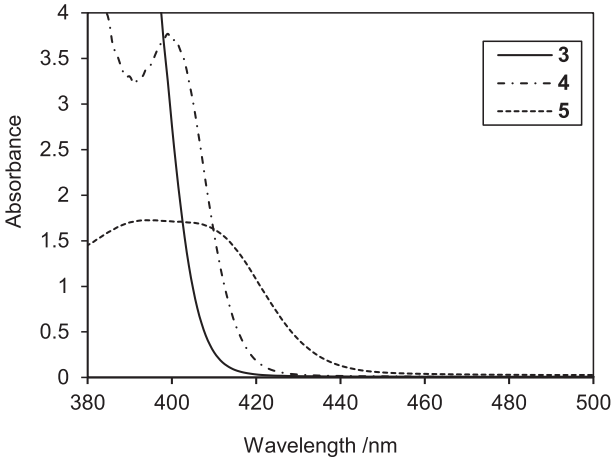
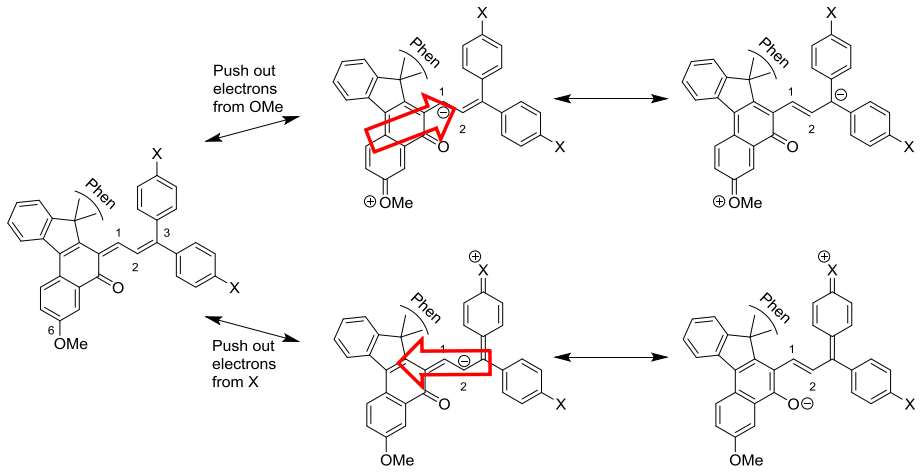


Fig. 7. Absorption spectra of **3**, **4** and **5** in toluene at 23 °C. Concentration: 5.0 × 10^{-4} mol dm^{-3}.



Scheme 5. Effect of electron-donating groups on C6 and C4′ of phenyl groups on C3 of **6** and **7** on resonance structures.

Table 5
Spectral data and fading rate data of **4**, **6** and **7** at 23 °C in toluene.

Naphthopyran	λ_{max}/nm	Absorbance of MC form	Fading rate	
			$t_{1/2}$/sec[a]	$t_{3/4}$/sec[a]
4	416	0.59	51	136
	549	0.87	57	197
6	466	0.16	6	13
	589	0.33	6	13
7	446	0.32	9	18
	567	0.48	9	19

[a] $t_{1/2}$: Half life time. $t_{3/4}$: Time required for three quarters of the initial absorbance disappears.

preparations required the removal of the isomers of **12** that do not have the methoxy group on C6. However, for **8**, the removal of the undesired isomer in **12** was unnecessary so that the chemical yield of the final compound was higher. Consequently, **8** was synthesized as shown in Scheme 3.

2.4.2. *Photochromism of **8***

As shown in Table 6 and Figs. 10 and 11, our molecular modification worked quite well. Although the fading rate of **8** became slower than **7**, it was still fast enough. As a result, coloration became

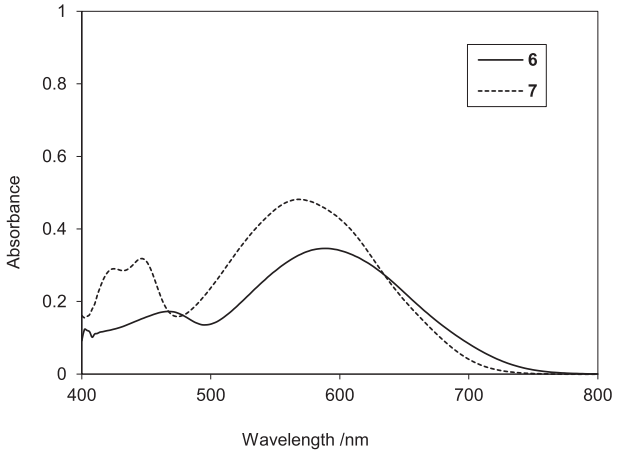


Fig. 8. Absorption spectra of MC form of **6** and **7** in toluene at 23 °C. Solvent and concentration: Toluene (5.8×10^{-3} mol dm^{-3}). Irradiation: Xenon lamp (300 nm – 500 nm based on ISO regulation).

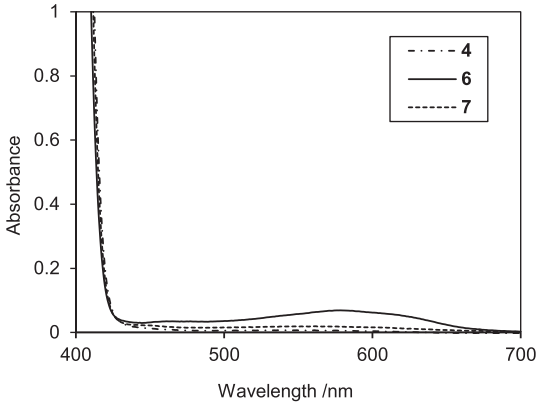
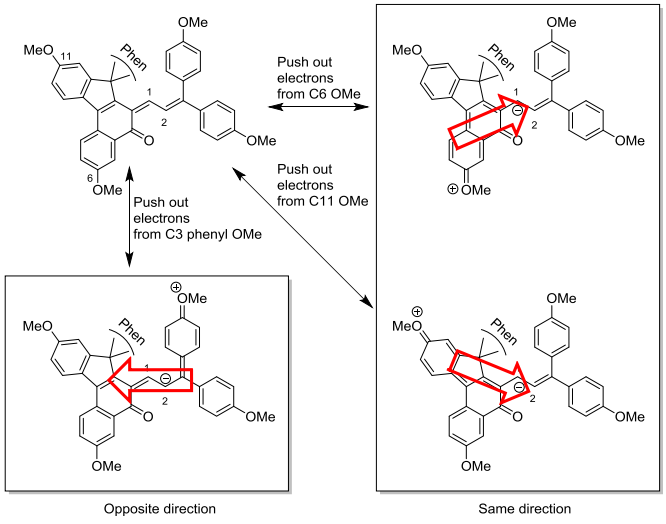


Fig. 9. Absorption spectra of NP form of **4**, **6** and **7** in toluene at 23 °C. Concentration: 5.0×10^{-4} mol dm^{-3}.

stronger and the idea to introduce electron-donating groups on both ends of the resonance structure to reduce the double bond character of the C1–C2 bond was also realized, as theorized. In addition, the maximum absorption wavelength of the longer absorption band shifted by 14 nm to a longer direction.



Scheme 6. Effect of methoxy groups on C6, C11 and C4′ of phenyl groups on C3 of **8** on resonance structures.

Table 6
Spectral data and fading rate data of **7** and **8** at 23 °C in toluene.

Naphthopyran	λ_{max}/nm	Absorbance of MC form	Fading rate	
			$t_{1/2}$/sec[a]	$t_{3/4}$/sec[a]
7	446	0.32	9	18
	567	0.48	9	19
8	429	0.40	14	29
	581	0.72	14	30

[a] $t_{1/2}$: Half life time. $t_{3/4}$: Time required for three quarters of the initial absorbance disappears.

We have, thus, developed an ideal photochromic dye **8** which can be applied to auto-color regulating ophthalmic lenses. Investigations of the photochromic properties of compound **8** and other related derivatives obtained in this work with polymer matrices are now underway in our laboratory.

3. Conclusion

Based on studies of molecular designs carried out with DFT calculations, we have synthesized naphthopyrans possessing a spiro-annulated phenanthrene ring with various electron-donating substituents on several carbon atoms. The introduction of methoxy groups on C6, C11, and C4′ of both phenyl groups on C3 worked effectively to control the fading rate, absorption wavelengths, and absorption intensities of longer and shorter absorption bands in the visible region. In particular, the naphthopyran dye **8** showed two absorption bands at 581 nm and 429 nm as the absorption maxima with absorbance of 0.72 and 0.40, respectively, under photo-irradiation conditions used in this research, as well as a fading rate (half lifetime) of 14 s at 23 °C in toluene.

4. Experimental

4.1. General

Chemical reactions were carried out under a dry nitrogen atmosphere. Dry tetrahydrofuran (THF) was purchased. All other solvents were used after drying with appropriate methods when necessary, otherwise used as received. All flash column chromatography were carried out on 230–400 mesh silica gel using ethyl acetate and hexane as eluent. Analytical thin-layer chromatography was performed on the pre-coated 0.25-mm thick silica gel TLC plates.

^{1}H NMR Spectra were recorded in deuteriochloroform ($CDCl_3$) unless otherwise described with a JEOL JNM-ECA400II 400 MHz NMR spectrometer. J values are expressed in Hz and quoted chemical shifts are in ppm. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. Infrared spectra (IR) were recorded on a PerkinElmer Spectrum One FT-IR Spectrometer. Mass spectra were measured by Waters Xevo G2-S QTof Ms LC-Ms system with 2695 separation modules. Analysis of the molecular ions was done with the atmospheric pressure chemical ionization (APCI) method by detecting $[M+1]^+$ ions. The LC was equipped with an Intersil ODS-3 column of GL Science, eluted with CH_3CN/H_2O = 80/20 solvent system with 1 ml min^{-1} flow rate.

Sample purity was examined with a Waters LC-53 equipped with an Intersil ODS-3 column, eluted with CH_3CN/H_2O = 80/20 solvent system with 1 ml min^{-1} flow rate.

UV and visible spectra were recorded on a Shimadzu UV-2550 spectrophotometer.

Melting points were measured using a Yanaco MP-S3 micro melting point system with the raising temperature of 2 °C min^{-1}, and those were uncorrected.

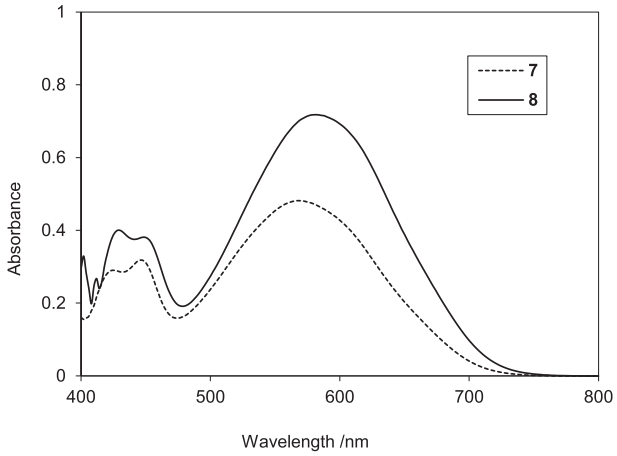


Fig. 10. Absorption spectra of MC form of **7** and **8** in toluene at 23 °C. Solvent and concentration: Toluene (5.8×10^{-3} mol dm^{-3}). Irradiation: Xenon lamp (300 nm – 500 nm based on ISO regulation).

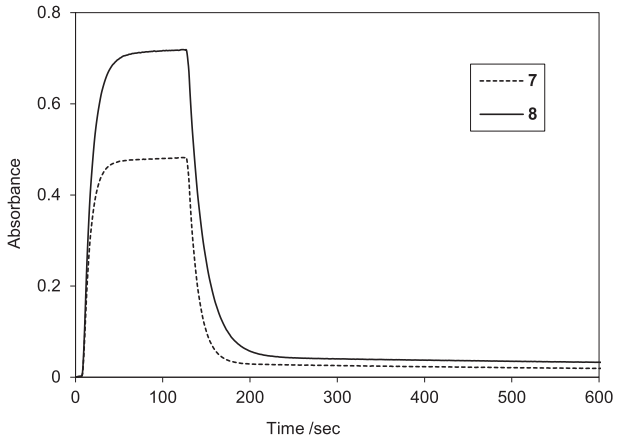


Fig. 11. Photocoloration and thermal fading of **7**, and **8** in toluene at 23 °C. Solvent and concentration: Toluene (5.8×10^{-3} mol dm^{-3}). Irradiation: Xenon lamp (300 nm – 500 nm based on ISO regulation). Detection wavelength: **7**: 567 nm; **8**: 581 nm.

DFT calculations were carried out with Spartan '8' or 14 provided by Wavefunction Inc. by B3LYP method with 6-31G* basis set.

Photoirradiation with UV and visible lights were carried out with the in-house-built equipment shown in Fig. 12.

The temperature inside the chamber was kept at 23 °C. The light source for irradiation was a 300 W xenon lamp with 50,000 lx in the range of 300–500 nm. The light was applied to the sample solution in a 1 mm thick quartz cell through an Air Mass Filter 2 so that the distribution of light intensity satisfied the ISO regulation [18]. Irradiation was continued for 120 s, and the fading behavior was monitored for 1200 s after the irradiation was stopped. Detection of change in absorbance was monitored with a multi-channel photodiode array spectrometer with a light from a 100 W halogen lamp equipped with a UV-cut filter. Data sampling interval was 1 s.

4.2. General methods for the preparation of 5-hydroxy-7H-benzo[c] fluoren-7-ones **12**

Synthesis of 5-hydroxy-7*H*-benzo[*c*]fluoren-7-ones **12** were performed according to the published procedures depicted in Scheme 3 [11].

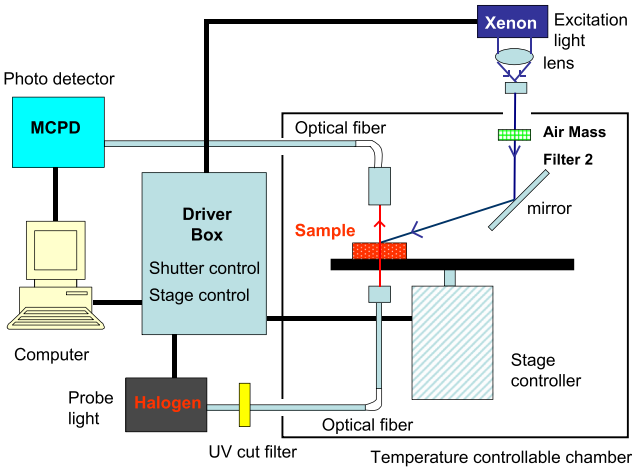


Fig. 12. Schematic diagram of the in-house-built apparatus for the assessment of photochromic properties of naphthopyrans.

4.3. *Preparation of naphthopyrans **3, 4, 6** and **7** (Scheme 3)*

The hydroxybenzofluorenones **12** were reacted with the propargyl alcohols **17** to give the naphthopyrans **13**. The naphthopyrans **13** were converted to the spiro[benzofluorenopyran-cyclopentaphenanthrene]s **3**, **4**, **6** and **7** by reacting with 4-lithiophenanthrene [19,20] followed by the treatment with p-TsOH.

4.3.1. *Synthesis of 3,3-diphenylbenzo [3,4] fluoreno[2,1-b]pyran-13(3H)-one **13**–**3***

To a refluxing solution of 5-hydroxy-7*H*-benzo[*c*]fluoren-7-one **12**–**3** (4.43 g, 17.99 mmol) in a mixture of toluene (180 mL) and 2-butanone (50 mL) were added 1,1-diphenylpropyn-1-ol (5.67 g, 27.2 mmol) and catalytic amount of p-TsOH, and the resulting mixture was refluxed for 2 h. The solution was cooled down to room temperature, then 10% aq. sodium hydroxide (21 mL), tetrahydrofuran (230 mL) and 10% aq. sodium chloride were added and the mixture was stirred well. The organic layer was separated, washed with water four times, and the solvent removed in vacuo. To the resulting residue was added acetone (90 mL) and the mixture was refluxed for 1.5 h. After the mixture was cooled down, the solid material precipitated was collected by filtration. After drying in vacuo, 3,3-diphenylbenzo[3,4]fluoreno[2,1-*b*]pyran-13(3*H*)-one **13**–**3** was obtained as a dark purple solid (3.91 g, 8.96 mmol) in 50% yield.

13–**3:** Mp 253–255 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 6.36 (1H, d, J = 10.4 Hz), 7.19 (1H, t, J = 8.0 Hz), 7.26 (4H, t, J = 6.8 Hz), 7.32 (4H, t, J = 7.2 Hz), 7.43 (1H, t, J = 8.0 Hz), 7.51 (4H, d, J = 8.8 Hz), 7.56 (3H, m), 7.86 (1H, d, J = 7.2 Hz), 7.91 (1H, d, J = 9.6 Hz), 8.38 (2H, m).

LC-MS Observed 437.1649 (M+1) (Calculated exact mass for $C_{32}H_{21}O_2$ (M+1) 437.1536).

FT-IR (KBr) ν/cm^{-1} 3054, 3026, 1700, 1601, 1490, 1463, 1398, 1369, 1338, 1274.

4.3.2. *Synthesis of 3,3-diphenyl spiro[benzo[3, 4] fluoreno[2,1-b] yran-13(3H),4′- [4H]cyclopenta[def]phenanthrene] **3***

A solution of 4-bromophenanthrene (384 mg, 1.5 mmol) in heptane (10 mL) was placed in a three-neck flask and was cooled down to 5 °C. To it was added a solution of 1.6 mol dm^{-3} butyllithium in hexane (0.94 mL, 1.5 mmol) gradually, and the resulting mixture was stirred at this temperature for 1 h. To this solution was added **13**–**3** (458 mg, 1.05 mmol) dissolved in 10 mL THF gradually, and the resulting mixture was stirred at this temperature for 1 h, and was warmed up gradually to room temperature in 3 h. The organic layer was separated, washed with water and sat. aq. sodium chloride, and the solvent removed in vacuo. The residue was purified with silica gel column chromatography (50 g, chloroform as eluent) to give the phenanthrene adduct (3,13-dihydro-3,3-diphenyl-13-(4-phenanthryl)benzo [3,4] fluoreno[2,1-*b*] pyran-13-ol) (440 mg, 0.72 mmol, 66%). After the phenanthrene adduct thus obtained (400 mg, 0.65 mmol) was dissolved in 20 mL toluene, a catalytic amount of p-TsOH was added and the solution was stirred at 75 °C for 2 h. The reaction mixture was washed with water and sat. aq. sodium chloride, and the solvent evaporated. The residue was purified with silica gel column chromatography (50 g, chloroform as eluent) followed by recrystallizations (from methanol then from acetonitrile) to give 3, 3- diphenyl spiro[benzo[3,4] fluoreno[2,1-*b*]pyran-13(3*H*),4′-[4*H*] cyclopenta[*def*] phenanthrene] **3** as a pale yellow solid (330 g, 0.55 mmol) in 85% yield.

3: Mp 209–212 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 5.11 (1H, d, J = 10.0 Hz), 5.33 (1H, d, J = 9.5 Hz), 6.44 (1H, d, J = 7.5 Hz), 6.95 (3H, m), 7.19 (10H, m), 7.37 (1H, t, J = 7.8 Hz), 7.54 (3H, m), 7.68 (1H, t, J = 7.8 Hz), 7.89 (2H, d, J = 8.0 Hz), 7.98 (2H, s). 8.32 (1H, d, J = 8.0 Hz), 8.45 (1H, d, J = 8.5 Hz), 8.78 (1H, d, J = 8.5 Hz).

LC-MS Observed 597.2282 (M+1) (Calculated exact mass for $C_{46}H_{29}O$ (M+1) 597.2213).

FT-IR (KBr) ν/cm^{-1} 3043, 1563, 1488, 1470, 1458, 1417, 1394, 1370, 1271.

4.3.3. *Synthesis of 6-methoxy-3, 3-diphenylbenzo [3,4] fluoreno [2,1-b] pyran-13(3H)-one **13**–**4***

To a refluxing solution of 5-hydroxy-3-methoxy-7H-benzo[*c*] fluoren-7-one **12**–**4** (5.0 g, 18.0 mmol) in a mixture of toluene (250 mL) and 2-butanone (50 mL) were added 1,1-diphenylpropyn-1-ol (5.62 g, 27.0 mmol) and catalytic amount of p-TsOH, and the resulting mixture was refluxed for 1 h. The solution was cooled down to room temperature, then 10% aq. sodium hydroxide (21 mL), tetrahydrofuran (260 mL) and 10% aq. sodium chloride were added and the mixture was stirred well. The organic layer was separated, washed with water four times, and the solvent removed in vacuo. To the resulting residue was added acetone (90 mL) and the mixture was refluxed for 1.5 h. After the mixture was cooled down, the solid material precipitated was collected by filtration. After drying in vacuo, 6-methoxy-3, 3-diphenylbenzo[3,4] fluoreno [2,1-*b*]pyran-13(3*H*)-one **13**–**4** was obtained as a dark purple solid (4.2 g, 9.0 mmol) in 50% yield.

13–**4**: Mp 209–212 °C.

^{1}H NMR ($CDCl_3$); δ/ppm 3.97 (3H, s), 6.34 (1H, d, J = 10.0 Hz), 7.21 (2H, m), 7.33 (6H, m), 7.41 (1H, t, J = 8.0 Hz), 7.50 (4H, d, J = 5.6 Hz), 7.57 (1H, d, J = 8.0 Hz), 7.62 (1H, d, J = 2.8 Hz), 7.81 (1H, d, J = 7.6 Hz), 7.90 (1H, d, J = 10.4 Hz), 8.29 (1H, d, J = 9.2 Hz).

LC-MS; Observed 467.1791 (M+1) (Calculated exact mass for $C_{33}H_{23}O_3$ (M+1) 467.1642).

FT-IR (KBr); ν/cm^{-1} 3054, 3014, 1697, 1616, 1490, 1463, 1433, 1419, 1401, 1372, 1274, 1226.

4.3.4. *Synthesis of 6- methoxy-3,3-diphenylspiro[benzo[3,4] fluoreno[2,1-b]pyran-13(3H),4′-[4H] cyclopenta[def] phenanthrene] **4***

A solution of 4-bromophenanthrene (350 mg, 1.36 mmol) in heptane (8 mL) was placed in a three-neck flask and was cooled down to 5 °C. To it was added a solution of 1.6 mol dm^{-3} butyllithium in hexane (0.88 mL, 1.4 mmol) gradually, and the resulting mixture was stirred at this temperature for 1 h. To this solution was added **13**–**4** (430 mg, 0.92 mmol) dissolved in 9 mL THF gradually, and the resulting mixture was stirred at this temperature for 1 h, and was warmed up gradually to room temperature in 2 h. The

organic layer was separated, washed with water and sat. aq. sodium chloride, and the solvent removed in vacuo. The residue was purified with silica gel column chromatography (50 g, chloroform as eluent) to give the phenanthrene adduct (3,13-dihydro-6-methoxy-3,3-diphenyl-13-(4-phenanthryl)benzo[3,4]fluoreno[2,1-*b*]pyran-13-ol) (360 mg, 0.56 mmol, 61%). After the phenanthrene adduct thus obtained (360 mg, 0.56 mmol) was dissolved in 50 mL toluene, 120 mg of p-TsOH was added and the solution was stirred at the refluxing temperature for 2 h. The reaction mixture was washed with water and sat. aq. sodium chloride, and the solvent evaporated. The residue was purified with silica gel column chromatography (50 g, chloroform as eluent) followed by recrystallization from acetonitrile to give 6-methoxy-3,3-diphenylspiro[benzo[3,4]fluoreno[2,1-*b*]pyran-13(3*H*),4′-[4*H*]cyclopenta[*def*]phenanthrene] **4** as a pale yellow solid (82 mg, 0.13 mmol) in 23% yield.

4: Mp 281–284 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 4.00 (3H, s), 5.11 (1H, d, J = 10.0 Hz), 5.32 (1H, d, J = 9.6 Hz), 6.43 (1H, d, J = 7.2 Hz), 6.95 (3H, m), 7.18 (10H, m), 7.35 (2H, m), 7.51 (2H, t, J = 3.8 Hz), 7.73 (1H, d, J = 2.8 Hz), 7.89 (2H, d, J = 7.6 Hz), 7.98 (2H, s), 8.26 (1H, d, J = 7.6 Hz), 8.70 (1H, d, J = 9.2 Hz).

LC-MS Observed 627.2021 (M+1) (Calculated exact mass for $C_{47}H_{31}O_2$ (M+1) 627.2319).

FT-IR (KBr) ν/cm^{-1} 3054, 1734, 1619, 1566, 1519, 1462, 1444, 1418, 1376, 1289.

4.3.5. Synthesis of 6-methoxy-3-(4-methoxyphenyl)-3-(4-morpholinophenyl)benzo[3,4]fluoreno[2,1-b]pyran-13(3H)-one ***13*–*6***

To a refluxing solution of 5-hydroxy-3-methoxy-7*H*-benzo[*c*]fluoren-7-one **12**–**4** (3.00 g, 10.9 mmol) in a mixture of toluene (123 mL) and 2-butanone (45 mL) were added 1-(4-methoxyphenyl)-1-(4-morpholinophenyl)propyn-1-ol (6.32 g, 19.56 mmol) and catalytic amount of p-TsOH, and the resulting mixture was refluxed for 10 min. The solution was cooled down to room temperature, then 10% aq. sodium hydroxide (21 mL), tetrahydrofuran (230 mL) and 10% aq. sodium chloride were added and the mixture was stirred well. The organic layer was separated, washed with water four times, and the solvent removed in vacuo. To the resulting residue was added acetone (90 mL) and the mixture was refluxed for 1 h. After the mixture was cooled down, the solid material precipitated was collected by filtration. After drying in vacuo, 6-methoxy-3-(4-methoxyphenyl)-3-(4-morpholinophenyl)benzo[3,4]fluoreno[2,1-*b*]pyran-13(3*H*)-one **13**–**6** was obtained as a dark purple solid (2.74 g, 4.70 mmol) in 43% yield.

13–**6**: Mp 191–193 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.14 (4H, t, J = 5.0 Hz), 3.77 (3H, s), 3.82 (4H, t, J = 5.0 Hz), 3.95 (3H, s), 6.27 (1H, d, J = 10.4 Hz), 6.84 (4H, m), 7.19 (2H, m), 7.39 (5H, m), 7.57 (2H, m), 7.81 (1H, d, J = 7.2 Hz), 7.85 (1H, d, J = 10.0 Hz), 8.27 (1H, d, J = 9.6 Hz).

LC-MS 582.2527 (M+1) (Calculated exact mass for $C_{38}H_{32}NO_5$ (M+1) 582.2275).

FT-IR (KBr) ν/cm^{-1} 3014, 2898, 2821, 1701, 1606, 1509, 1462, 1428, 1372, 1275, 1221.

4.3.6. Synthesis of 6-methoxy-3-(4-methoxyphenyl)-3-(4-morpholinophenyl)spiro[benzo[3,4]fluoreno[2,1-b]pyran-13(3H),4′-[4H]cyclopenta[def] phenanthrene] ***6***

A solution of 4-bromophenanthrene (490 mg, 1.90 mmol) in heptane (12 mL) was placed in a three-neck flask and was cooled down to 0 °C. To it was added a solution of 1.6 mol dm^{-3} butyllithium in hexane (0.9 mL, 1.44 mmol) gradually, and the resulting mixture was stirred at this temperature for 3 h. To this solution was added **13**–**6** (640 mg, 1.1 mmol) dissolved in 12 mL THF gradually, and the resulting mixture was stirred at this temperature for 1 h, and was warmed up gradually to room temperature in 5 h. The organic layer was separated, washed with water and sat. aq. sodium chloride, and the solvent removed in vacuo. The residue was purified with silica gel column chromatography (50 g, chloroform as eluent) to give the phenanthrene adduct (3,13-dihydro-6-methoxy-3-(4-methoxyphenyl)-3-(4-morpholinophenyl)-13-(4-phenanthryl)benzo[3,4]fluoreno[2,1-*b*]pyran-13-ol) (260 mg, 0.34 mmol, 31%). After the phenanthrene adduct thus obtained (260 mg, 0.34 mmol) was dissolved in 25 mL toluene, 9 mg of p-TsOH was added and the solution was stirred at the refluxing temperature for 2 h. The reaction mixture was washed with water and sat. aq. sodium chloride, and the solvent evaporated. The residue was purified with silica gel column chromatography (50 g, chloroform as eluent) followed by recrystallization from acetonitrile and from toluene to give 6-methoxy-3-(4-methoxyphenyl)-3-(4-morpholinophenyl)spiro[benzo[3,4]fluoreno[2,1-*b*]pyran-13(3*H*),4′-[4*H*]cyclopenta[*def*]phenanthrene] **6** as a violet solid (170 mg, 0.23 mmol) in 68% yield.

6: Mp 204–207 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.09 (4H, t, J = 4.8 Hz), 3.72 (3H, s), 3.79 (4H, t, J = 4.8 Hz), 5.05 (1H, d, J = 10.0 Hz), 5.24 (1H, d, J = 10.0 Hz), 6.42 (1H, d, J = 7.6 Hz), 6.68 (2H, d J = 1.2 Hz), 6.71 (2H, d, J = 0.8 Hz), 6.93 (1H, t, J = 3.8 Hz), 6.98 (2H, d, J = 7.2 Hz), 7.09 (4H, m), 7.35 (2H, m), 7.51 (2H, t, J = 3.8 Hz), 7.69 (1H, d, J = 2.8 Hz), 7.89 (2H, d, J = 8.0 Hz), 7.98 (2H, s), 8.26 (1H, d, J = 8.0 Hz), 8.69 (1H, d, J = 9.2 Hz).

LC-MS *m*/*z* 742.2607 (M+1) (Calculated exact mass for $C_{52}H_{40}NO_4$ (M+1) 742.2952).

FT-IR (KBr) ν/cm^{-1} 3062, 2956, 2833, 1607, 1583, 1508, 1462, 1417, 1397, 1374, 1304, 1289.

4.3.7. Synthesis of 6-methoxy-3,3-bis(4-methoxyphenyl)benzo[3,4]fluoreno[2,1-b]pyran-13(3H)-one ***13*–*7***

To a refluxing solution of 5-hydroxy-3-methoxy-7*H*-benzo[*c*]fluoren-7-one **12**–**4** (3.00 g, 10.9 mmol) in a mixture of toluene (123 mL) and 2-butanone (45 mL) were added 1,1-bis(4-methoxyphenyl)propyn-1-ol (5.23 g, 19.5 mmol) and catalytic amount of p-TsOH, and the resulting mixture was refluxed for 30 min. The solution was cooled down to room temperature, then 10% aq. sodium hydroxide (21 mL), tetrahydrofuran (120 mL) and 10% aq. sodium chloride were added and the mixture was stirred well. The organic layer was separated, washed with water four times, and the solvent removed in vacuo. To the resulting residue was added acetone (100 mL) and the mixture was refluxed for 1 h. After the mixture was cooled down, the solid material precipitated was collected by filtration. After drying in vacuo, 6-methoxy-3,3-bis(4-methoxyphenyl)benzo[3,4]fluoreno[2,1-*b*]pyran-13(3*H*)-one **13**–**7** was obtained as a dark purple solid (2.47 g, 4.70 mmol) in 43% yield.

13–**7**: Mp 207–209 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.77 (3H, s), 3.96 (3H, s), 6.27 (1H, d, J = 10.0 Hz), 6.84 (4H, m), 7.20 (2H, m), 7.40 (5H, m), 7.57 (2H, m), 7.80 (1H, d, J = 8.0 Hz), 7.86 (1H, d, J = 10.0 Hz), 8.27 (1H, d, J = 9.2 Hz).

LC-MS 527.2033 (M+1) (Calculated exact mass for $C_{35}H_{27}O_5$ (M+1) 527.1853).

FT-IR (KBr) ν/cm^{-1} 3014, 2953, 2831, 1695, 1605, 1505, 1466, 1397, 1373, 1277, 1218.

4.3.8. Synthesis of 6-methoxy-3,3-bis(4-methoxyphenyl)spiro[benzo[3,4]fluoreno[2,1-b]pyran-13(3H),4′-[4H]cyclopenta[def] phenanthrene] ***7***

A solution of 4-bromophenanthrene (440 mg, 1.72 mmol) in heptane (30 mL) was placed in a three-neck flask and was cooled

down to −78 °C. To it was added a solution of 1.6 mol dm^{-3} butyllithium in hexane (1.9 mL, 1.6 mmol) gradually, and the resulting mixture was stirred at this temperature for 1 h. To this solution was added **13**–**7** (550 mg, 1.04 mmol) dissolved in 150 mL THF gradually, and the resulting mixture was stirred at this temperature for 1 h, and was warmed up gradually to room temperature in 5 h. The organic layer was separated, washed with water and sat. aq. sodium chloride, and the solvent removed in vacuo. The residue was purified with silica gel column chromatography (50 g, chloroform as eluent) to give the phenanthrene adduct (3,13-dihydro-6-methoxy-3,3-bis(4-methoxyphenyl)-13-(4-phenanthryl)benzo[3,4]fluoreno[2,1-*b*]pyran-13-ol) (200 mg, 0.28 mmol, 27%). After the phenanthrene adduct thus obtained (200 mg, 0.28 mmol) was dissolved in 30 mL toluene, 9 mg of p-TsOH was added and the solution was stirred at the refluxing temperature for 2 h. The reaction mixture was washed with water and sat. aq. sodium chloride, and the solvent evaporated. The residue was purified with silica gel column chromatography (50 g, chloroform as eluent) followed by recrystallization from acetonitrile and from toluene to give 6-methoxy-3,3-bis(4-methoxyphenyl)spiro[benzo[3,4]fluoreno[2,1-*b*]pyran-13(3*H*),4′-[4*H*]cyclopenta[*def*]phenanthrene] **7** as a pale yellow solid (92 mg, 0.13 mmol) in 46% yield.

7: Mp 199–202 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.72 (6H, s), 3.98 (3H, s), 5.06 (1H, d, J = 10.0 Hz), 5.25 (1H, d, J = 9.6 Hz), 6.42 (1H, d, J = 6.8 Hz), 6.69 (2H, d J = 2.4 Hz), 6.71 (2H, d, J = 2.4 Hz), 6.93 (1H, t, J = 3.8 Hz), 6.98 (2H, d, J = 7.2 Hz), 7.09 (4H, m), 7.35 (2H, m), 7.51 (2H, t, J = 3.8 Hz), 7.69 (1H, d, J = 2.8 Hz), 7.89 (2H, d, J = 8.4 Hz), 7.98 (2H, s), 8.27 (1H, d, J = 7.6 Hz), 8.69 (1H, d, J = 9.6 Hz).

LC-MS 687.2227 (M+1) (Calculated exact mass for $C_{49}H_{35}O_4$ (M+1) 687.2530).

FT-IR (KBr) ν/cm^{-1} 3038, 2956, 2833, 1607, 1584, 1564, 1508, 1431, 1398, 1373, 1298.

4.4. General methods for the preparation of naphthopyrans ***5*** and ***8*** (Scheme 3)

The hydroxy group of each 5-hydroxy-7*H*-benzo[*c*]fluoren-7-one **12** was protected as the benzyl ether, then it was reacted with 4-lithiophenanthrene, deprotected, and dehydrated to form spiro(benzofluorene-cyclopentaphenanthrene) **16**. The naphthopyrans **5** and **8** were finally constructed by the reaction of **16** with diphenylpropargyl alcohols **17** [21].

4.4.1. Synthesis of 5-benzyloxy-3-(4-morpholinyl)-7H-benzo[c]fluoren-7-one ***14***–***5***

To the solution of 5-hydroxy-3-(4-morpholinyl)-7*H*-benzo[*c*]fluoren-7-one **12**–**5** (8.33 g, 25 mmol) in dry DMF (150 ml) were added benzyl chloride (6.40 g, 50 mmol) and K_2CO_3 (9.66 g, 70 mmol) and the mixture was kept at 60 °C for 3 h. The solution was cooled down to room temperature, then water (150 mL), tetrahydrofuran (300 mL) and toluene (300 mL) were added and the mixture was stirred well. The organic layer was separated, washed with sat. aq. sodium chloride two times, and the solvent removed in vacuo. To the resulting residue was added methanol (100 mL) and the mixture was stirred for 1 h. The solid material precipitated was collected by filtration. After drying in vacuo, 5-benzyloxy-3-(4-morpholinyl)-7*H*-benzo[*c*]fluoren-7-one **14**–**5** was obtained as a red solid (4.33 g, 0.10 mmol) in 40% yield.

14–**5**: Mp 241–243 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.35 (4H, t, J = 4.8 Hz), 3.92 (4H, t, J = 4.8 Hz), 5.31 (1H, s), 7.14 (1H, s), 7.20 (1H, t, J = 7.4 Hz), 7.37 (2H, m), 7.43 (3H, t, J = 7.8 Hz), 7.55 (2H, d, J = 18.8 Hz), 7.59 (1H, d, J = 9.6 Hz), 7.61 (1H, s), 7.83 (1H, d, J = 7.2 Hz), 8.33 (1H, d, J = 9.2 Hz)

LC-MS Observed 422.1731 (M+1) (Calculated exact mass for $C_{28}H_{24}NO_3$ (M+1) 422.1751).

FT-IR (KBr) ν/cm^{-1} 1697, 1618, 1574, 1464, 1455, 1419, 1395, 1370, 1345, 1278.

4.4.2. Synthesis of 3-(4-morpholinyl)-7-(4-phenanthryl)-7H-benzo[c]fluorene-5,7-diol ***15***–***5***

To the solution of 4-bromophenanthrene (2.88 g, 11.3 mmol) in dry THF (100 mL) cooled to −78 °C was added 1.6 mol dm^{-3} butyllithium in hexane (5.6 mL, 9 mmol) gradually to give 4-lithiophenanthrene. It was gradually added to the THF (300 mL) solution of **14**–**5** (2.9 g, 6.8 mmol) at −78 °C, and the resulting mixture was stirred for 1 h, then water (150 mL) and toluene (400 mL) were added and the mixture was stirred well. The organic layer was separated, washed with sat. aq. sodium chloride two times, and the solvent removed in vacuo. The residue was purified by silica gel column chromatography (300 g, $CHCl_3$/ethyl acetate = 90/10 v/v) two times to give the phenanthrene adduct (5-benzyloxy-3-(4-morpholino)-7-(4-phenanthryl)-7*H*-benzo[*c*]fluoren-7-ol) as a pink solid (2.0 g, 3.3 mmol, yield 48%).

The phenanthrene adduct (1.0 g, 1.7 mmol) thus obtained was added to the mixture of 5% Pd/C (0.8 g, 50 wt% water contained), ammonium formate (0.8 g, 12.7 mmol) and THF (30 mL), and the resulting mixture was stirred for 2 h. Pd/C was filtered off and the solvent removed in vacuo. The residue was dissolved in a mixture of THF (100 mL) and toluene (100 mL), which was washed with sat. aq. sodium chloride two times. The solvent was removed in vacuo to give 3-(4-morpholinyl)-7-(4-phenanthryl)-7*H*-benzo[*c*]fluorene-5,7-diol **15**–**5** as a yellow solid (1.4 g, 2.7 mmol) in 40% yield.

15–**5**: Mp 251–253 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.29 (4H, t, J = 4.8 Hz), 3.86 (4H, t, J = 4.8 Hz), 6.32 (1H, t, J = 7.6 Hz), 6.58 (1H, s), 6.93 (1H, t, J = 7.4 Hz), 7.09 (2H, m), 7.32 (1H, t, J = 7.2 Hz), 7.45 (1H, d, J = 8.0 Hz), 7.56 (4H, m), 7.74 (1H, d, J = 8.8 Hz), 7.84 (1H, t, J = 8.0 Hz), 7.96 (1H, d, J = 7.2 Hz), 8.27 (1 h, d, J = 7.6 Hz), 8.70 (1H, d, J = 9.6 Hz), 9.04 (1H. d, J = 7.6 Hz)

LC-MS Observed 510.2208 (M+1) (Calculated exact mass for $C_{35}H_{28}NO_3$ (M+1) 510.2064).

FT-IR (KBr) ν/cm^{-1} 3375, 3047, 2960, 2922, 2857, 1693, 1623, 1588, 1578, 1519, 1481, 1449, 1417, 1376, 1244.

4.4.3. Synthesis of 3-(4-morpholinyl)spiro[7H-benzo[c]fluorene-7,4′[4H]cyclopenta[def]phenanthren]-5-ol ***16***–***5***

To the toluene (50 mL) solution of **15**–**5** (2.0 g, 3.3 mmol) was added a small amount of p-TsOH, and the resulting solution was refluxed for 10 h. After it was cooled down to room temperature, the reaction mixture was washed with sat. aq. sodium chloride, and the solvent removed in vacuo. The residue was dispersed in chloroform (20 mL) and stirred for a while, and the suspending solid material was recovered by filtration to give 3-(4-morpholinyl)spiro[7*H*-benzo[*c*]fluorene-7,4′[4*H*]cyclopenta[*def*]phenanthren]-5-ol **16**–**5** as a gray solid (300 mg, 0.61 mmol) in 18% yield.

16–**5**; Mp 290–293 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.29 (4H, t, J = 4.8 Hz), 3.86 (4H, t, J = 4.8 Hz), 6.56 (1H, d, J = 8.0 Hz), 6.96 (2H, d, J = 7.2 Hz), 7.04 (1H, t, J = 4.2 Hz), 7.46 (1H, t, J = 8.0 Hz), 7.54 (2H, t, J = 7.4 Hz), 7.62 (2H, m), 7.92 (1H, s), 7.94 (1H, s), 8.00 (1H, s), 8.41 (1H, d, J = 8.0 Hz), 8.80 (1H, d, J = 9.2 Hz)

LC-MS Observed 492.2149 (M+1) (Calculated exact mass for $C_{35}H_{26}NO_2$ (M+1) 492.1958).

FT-IR (KBr) ν/cm^{-1} 3243, 2956, 2345, 1684, 1624, 1591, 1521, 1485, 1415, 1377, 1238, 1220.

*4.4.4. Synthesis of 6-(4-morpholinyl)-3,3-diphenylspiro[benzo[3,4] fluoreno[2,1-b]pyran-13(3H),4′-[4H]cyclopenta[def]phenanthrene] **5***

To the solution of **16**–**5** (120 mg, 0.24 mmol) in toluene (120 ml) were added 1,1-diphenylpropyn-1-ol (77 mg, 0.37 mmol) and catalytic amount of p-TsOH, and the resulting mixture was heated at 80 °C for 18 h. The reaction mixture was washed with sat. aq. sodium chloride three times, and the solvent removed in vacuo. The residue was purified by silica gel column chromatography (100 g, 90/10 $CHCl_3$/ethyl acetate as eluent) two times, and by HPLC (column: Intersil ODS-3 (GL Science), elution: 90/10 CH_3CN/H_2O) to give 6-(4-morpholinyl)-3,3-diphenylspiro[benzo[3,4]fluoreno[2,1-*b*]pyran-13(3*H*),4′-[4*H*]cyclopenta[*def*]phenanthrene] **5** as a brown solid (32 mg, 0.047 mmol) in 20% yield.

5: Mp 171–178 °C.

^{1}H NMR (DMSO-d_6) δ/ppm 3.36 (4H, t, J = 4.0 Hz), 3.87 (4H, t, J = 4.0 Hz), 4.99 (1H, d, J = 10.0 Hz), 5.72 (1H, d, J = 10.0 Hz), 6.28 (1H, d, J = 6.8 Hz), 6.90 (2H, d, J = 6.8 Hz), 7.00 (1H, t, J = 3.8 Hz), 7.23 (11H, m), 7.37 (1H, t, J = 3.9 Hz), 7.60 (3H, m), 8.03 (2H, d, J = 8.4 Hz), 8.09 (2H, s), 8.42 (1H, d, J = 8.4 Hz), 8.77 (1H, d, J = 10.0 Hz).

LC-MS Observed 682.2541(M+1) (Calculated exact mass for $C_{50}H_{36}NO_2$ (M+1) 682.2741).

FT-IR (KBr) ν/cm^{-1} 3049, 2923, 2853, 1615, 1584, 1557, 1515, 1462, 1443, 1401, 1260.

*4.4.5. Synthesis of 5-benzyloxy-3,9-dimethoxy-7H-benzo[c]fluoren-7-one **14**–**8***

To the dry DMF (150 mL) solution of 5-hydroxy-3,9-dimethoxy-7*H*-benzo[*c*]fluoren-7-one **12**–**8** (7.6 g, 25 mmol) were added benzyl chloride (6.40 g, 50 mmol) and K_2CO_3 (9.66 g, 70 mmol), and the resulting mixture was kept at 60 °C for 3 h. The solution was cooled down to room temperature, then water (150 mL), tetrahydrofuran (300 mL) and toluene (300 mL) were added and the mixture was stirred well. The organic layer was separated, washed with sat. aq. sodium chloride two times, and the solvent removed in vacuo. To the resulting residue was added methanol (100 mL) and the mixture was stirred for 1 h. The solid material precipitated was collected by filtration. After drying in vacuo, 5-benzyloxy-3,9-dimethoxy-7*H*-benzo[*c*]fluoren-7-one **14**–**8** was obtained as a red solid (7.9 g, 20 mmol) in 80% yield.

14–**8**: Mp 185–187 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.86 (3H, s), 3.94 (3H, s), 6.89 (1H, d, J = 11.2 Hz), 7.18 (1H, d, J = 2.4 Hz), 7.25 (3H, m), 7.36 (1H, m), 7.43 (2H, t, J = 8.0 Hz), 7.52 (2H, d, J = 7.2 Hz), 7.63 (1H, d, J = 2.8 Hz), 7.69 (1H, d, J = 8.0 Hz), 8.24 (1H, d, J = 8.0 Hz).

LC-MS Observed 397.1489 (M+1) (Calculated exact mass for $C_{26}H_{21}O_4$ (M+1) 397.1434).

FT-IR (KBr) ν/cm^{-1} 1699, 1606, 1574, 1481, 1462, 1430, 1367, 1265, 1218.

*4.4.6. Synthesis of 3,9-dimethoxy-7-(4-phenanthryl)-7H-benzo[c] fluorene-5,7-diol **15**–**8***

To the dry THF solution (100 mL) of 4-bromophenanthrene (2.88 g, 11.3 mmol) at −78 °C was added 1.6 mol dm^{-3} butyllithium in hexane (5.6 mL, 9 mmol) gradually to give 4-lithiophenanthrene. It was gradually added to **14**–**8** (3.0 g,7.6 mmol) dissolved in dry THF (300 ml) cooled to −78 °C, and the solution was stirred for 1 h, then water (150 mL) and toluene (400 mL) were added and the mixture stirred well. The organic layer was separated, washed with sat. aq. sodium chloride two times, and the solvent removed in vacuo. The residue was purified by silica gel column chromatography (300 g, 90/10 $CHCl_3$/ethyl acetate as eluent) two times to give the phenanthrene adduct (5-benzyloxy-3,9-dimethoxy-7-(4-phenanthryl)-7*H*-benzo[*c*]fluoren-7-ol) as a pink solid (1.9 g, 3.3 mmol) in 43% yield.

The phenanthrene adduct (1.0 g, 1.7 mmol) thus obtained was added to the mixture of 5% Pd/C (0.8 g, 50 wt% water contained), ammonium formate (0.8 g, 12.7 mmol) and THF (30 mL), and the resulting mixture was stirred for 2 h. Pd/C was filtered off and the solvent removed in vacuo. The residue was dissolved in a mixute of THF (100 mL) and toluene (100 mL), which was washed with sat. aq. sodium chloride two times. The solvent was removed in vacuo to give 3,9-dimethoxy-7-(4-phenanthryl)-7*H*-benzo[*c*]fluorene-5,7-diol **15**–**8** as a yellow solid (1.45 g, 3.0 mmol) in 40% yield.

15–**8**: Mp 219–221 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.53 (3H,s), 3.89 (3H, s), 6.31 (1H, t, J = 7.6 Hz), 6.60 (2H, d, J = 11.6 Hz), 6.86 (1H, d, J = 6.4 Hz), 6.99 (1H, t, J = 7.9 Hz), 7.32 (1H, d, J = 9.2 Hz), 7.43 (1H, d, J = 8.0 Hz), 7.54 (3H, m), 7.70 (1H, d, J = 8.8 Hz), 7.80 (1H, t, J = 9.6 Hz), 7.93 (1H, d, J = 7.2 Hz), 8.16 (1H, d, J = 8.4 Hz), 8.64 (1H, d, J = 9.2 Hz), 9.00 (1H, d, J = 7.6 Hz)

LC-MS Observed 485.1892 (M+1) (Calculated exact mass for $C_{33}H_{25}O_4$ (M+1) 485.1747).

FT-IR (KBr) ν/cm^{-1} 3346, 1594, 1524, 1483, 1423, 1383, 1361, 1267, 1215.

*4.4.7. Synthesis of 3,9-dimethoxyspiro[7H-benzo[c]fluorine-7,4′ [4H]cyclopenta[def]phenanthren]-5-ol **16**–**8***

To the toluene (50 mL) solution of **15**–**8** (1.0 g, 1.7 mmol) was added a small amount of p-TsOH, and the resulting solution was refluxed for 10 h. After it was cooled down to room temperature, the reaction mixture washed with sat. aq. sodium chloride, and the solvent removed in vacuo. The residue was dispersed in chloroform (20 ml) and stirred for a while, then filtered to give 3,9-dimethoxyspiro[7*H*-benzo[*c*]fluorene-7,4′[4*H*]cyclopenta[*def*]phenanthren]-5-ol **16**–**8** as a gray solid (650 mg, 1.4 mmol) in 82% yield.

16–**8**: Mp 186–188 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.56 (3H, s), 3.94 (3H, s), 5.91 (1H, s), 6.18 (1H, d, J = 2.8 Hz), 6.99 (2H, d, J = 7.2 Hz), 7.03 (1H, d, J = 8.8 Hz), 7.44 (1H, d, J = 8.0 Hz), 7.54 (2H, t, J = 7.6 Hz), 7.64 (1H, d, J = 2.4 Hz), 7.92 (2H, d, J = 8.0 Hz), 8.03 (2H, s), 8.33 (1H, d, J = 8.8 Hz), 8.77 (1H, d, J = 9.2 Hz).

LC-MS Observed 467.1823 (M+1) (Calculated exact mass for $C_{33}H_{23}O_3$ (M+1) 467.1642).

FT-IR (KBr) ν/cm^{-1} 3382, 3012, 2936, 1692, 1594, 1580, 1523, 1478, 1433, 1416, 1270, 1218.

*4.4.8. Synthesis of 6,11-dimethoxy-3,3-bis(4-methoxyphenyl)spiro [benzo[3,4]fluoreno[2,1-b]pyran-13(3H),4′-[4H]cyclopenta[def] phenanthrene] **8***

To the solution of **16**–**8** (466 mg, 1.0 mmol) in toluene (120 ml) were added 1,1-bis(4-methoxyphenyl)propyn-1-ol (376 mg, 1.40 mmol) and catalytic amount of p-TsOH, and the resulting mixture was heated at 80 °C for 30 min. The reaction mixture was washed with sat. aq. sodium chloride three times, and the solvent removed in vacuo. The residue was purified by silica gel column chromatography (100 g, 90/10 $CHCl_3$/ethyl acetate as eluent) two times and recrystallization from a mixture of toluene and ethyl acetate to give 6,11-dimethoxy-3,3-bis(4-methoxyphenyl)spiro [benzo[3,4]fluoreno[2,1-*b*]pyran-13(3*H*),4′-[4*H*]cyclopenta[*def*] phenanthrene] **8** as a pale yellow solid (315 mg, 0.44 mmol) in 44% yield.

8: Mp 252–254 °C.

^{1}H NMR ($CDCl_3$) δ/ppm 3.53 (3H, s), 3.72 (6H, s), 3.97 (3H, s), 5.02 (1H, d, J = 10.0 Hz), 5.23 (1H, d, J = 9.6 Hz), 5.98 (1H, d, J = 2.0 Hz), 6.68 (2H, d, J = 1.6 Hz), 6.70 (2H, d, J = 1.6 Hz), 6.90 (1H, d, J = 11.0 Hz), 6.99 (2H, d, J = 7.2 Hz), 7.09 (4H, m), 7.31 (1H, d,

J = 9.2 Hz), 7.51 (2H, t, J = 3.8 Hz), 7.67 (1H, d, J = 2.4 Hz), 7.89 (2H, d, J = 8.0 Hz), 7.97 (2H, s), 8.16 (1H, d, J = 8.8 Hz), 8.62 (1H, d, J = 9.2 Hz).

LC-MS Observed 717.2347 (M+1) (Calculated exact mass for $C_{50}H_{37}O_5$ (M+1) 717.2636).

FT-IR (KBr) ν/cm^{-1} 3038, 2999 2931, 2832, 1606, 1584, 1508, 1455, 1418, 1355, 1299.

Acknowledgments

The authors are grateful to Tokuyama Corp. for supporting this work and permitting us the publication of results obtained.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.03.019.

References

[1] Van Gemert B. Benzo and naphthopyrans (chromens). In: Crano JC, Guglielmetti R, editors. Organic photochromic and thermochromic compounds, Vol. 1. New York: Plenum Press; 1999. p. 111–40 [Chapter 3].
[2] Hepworth JD, Heron BM. Photochromic naphthopyrans. In: Kim S-H, editor. Functional dyes. Oxford: Elsevier; 2006. p. 85–135 [Chapter 3].
[3] Becker RS, Michl J. Photochromism of synthetic and naturally occurring 2H-chromenes and 2H-pyrans. J Am Chem Soc 1969;88:5931–3.
[4] Van Gemert B, Kumar A, Knowles DB. Naphthopyrans. Structural features and photochromic properties. Mol Cryst Liq Cryst 1997;297:131–8.
[5] Van Gemert B. The commercialization of plastic photochromic lenses: a tribute to John Crano. Mol Cryst Liq Cryst 2000;344:57–62.
[6] Delbaere S, Luccioni-Houze B, Bochu C, Teral Y, Campredon M, Vermeersch G. Kinetic and structural studies of the photochromic process of 3H-naphthopyrans by UV and NMR spectroscopy. J Chem Soc Perkin Trans 1998;2:1153–8.
[7] Song L, Yang Y, Zhang Q, Tian H, Zhu W. Synthesis and photochromism of naphthopyrans bearing naphthalimide chromophore: predominant thermal reversibility in color-fading and fluorescence switch. J Photochem Photobiol A Chem 2011;115:14648–58.
[8] Aiken S, Booth K, Gabbutt CD, Heron BM, Rice CR, Charaf-Eddin A, et al. The first structural and spectroscopic characterisation of a ring-opened form of a 2*H*-naphtho[1,2-*b*]pyran: a novel photomerocyanine. Chem Commun 2014;50:7900–3.
[9] Tanizawa T, Hara T, Kawabata Y, Momoda J, Nagoh H. Chromene compounds. U. S Pat 2001;6,197,225.
[10] Clarke DA, Heron BM, Gabbutt CD, Hepworth JD, Partington SM, Corns SN. pH sensitive photochromic dyes. US Pat 1999;WO99/031081.
[11] Kumar A, Van Gemert B, Knowles DB. Substituted naphthopyrans. US Pat 1995;5,458,814.
[12] Clarke DA, Heron BM, Gabbutt CD, Hepworth JD, Partington SM, Corns SN. Photochromic substituted 2H-naphtho[1,2-b]pyrans. WO00/35902.
[13] Van Gemert B. Novel photochromic indeno-fused naphthopyrans. U. S Pat 1996;5,645,767;WO96/14596.
[14] DFT calculations were carried out using Spartan'8 and Spartan'14 (Wavefunction) with P3LYP/6-31G* in vacuum.
[15] Dyllick-Brenzinger R, Baus U. Preparation of beta-naphthyl benzyl ether, U. S Pat 1994;5,352,843.
[16] Yokoyama Y, Sagisaka T, Mizuno Y, Yokoyama Y. Role of the methoxy substituents on the photochromic indolylfulgides. Absorption maximum *vs.* molar absorption coefficient of the colored form. Chem Lett 1996;25:1037–8.
[17] Gushiken T, Saito M, Ubukata T, Yokoyama Y. Fast decoloration of spironaphthooxazine bound to a poly(dimethylsiloxane) network. Photochem Photobiol Sci 2010;9:162–9.
[18] ISO 8980-3. Ophthalmic optics uncut finished spectacle lenses, Part 3. Transmittance specifications and test methods. 2nd ed. 2003.
[19] Kajigaeshi S, Kadowaki T, Nishida A, Fuzisaki S. Selective preparation of fluorene derivatives using the t-butyl function as positional protective group. Bull Chem Soc Jpn 1986;59:97–103.
[20] Newman MS, Patrick TB, Darlak RS, Zuech EA. Synthesis of 4-bromophenanthrene. J Org Chem 1969;34:1904–6.
[21] Nakatsuji S, Narashima K, Iyoda M, Akiyama S. A simple and convenient synthesis of aryl-substituted push-pull butadienes from 1,1-diaryl-2-propyn-1-ols. Bull Chem Soc Jpn 1988;61:2253–5.