



# Photochromism

# Remarkable Influence of Phenyl/Arylethynylation on the Photochromism of 2,2-Diphenylbenzopyrans (Chromenes)

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**Abstract:** Phenyl/arylethynylation of 2,2-diphenylbenzopyrans (i.e., chromenes) permits modulation of the spectral properties of photogenerated colored *o*-quinonoid intermediates, and brings about remarkable stabilization of the latter, rendering the phenomenon of photochromism observable readily at room temperature. Modification of the spectrokinetic properties of the *o*-quinonoid intermediates are a consequence of resonance effects, with the substituent effects being relayed nicely from one end of the molecule to the other. Functionalization at

the 6-position of the chromene nucleus leads to more redshifted absorptions as well as to increased lifetimes of the colored species when compared with functionalization at the 7position. Given that photochromism is observable in the parent chromene at only low temperatures, phenyl/arylethynylation, which precludes steric inhibition of resonance, is demonstrated to render bleaching kinetics of the colored intermediates that approach those reported for industrially relevant diarylnaphthopyrans.

## Introduction

The design and synthesis of molecular systems that respond to light and heat as external stimuli constitutes an important area in the development of organic photochromic materials, which are of paramount importance in variable-transmission glasses, molecular switches, nanoscale machines, high-density optical storage, imaging devices, smart windows and biological phenomena such as photomorphogenesis and vision process.<sup>[1,2]</sup> Among the known photochromic systems,<sup>[1,2]</sup> photochromic diaryInaphthopyrans, which belong to the class of chromenes (i.e., 2,2-diaryl-2H-1-benzopyrans), are of particular importance because of their practical utility in ophthalmic lenses.<sup>[3]</sup> In general, photoirradiation of colorless pyrans (closed forms) results in heterolytic cleavage of the C(sp<sup>3</sup>)-O bond in their singlet excited states, leading to formation of colored o-quinonoid intermediates (open forms).<sup>[4]</sup> The latter may revert to the initial colorless closed forms either thermally or photochemically with visible light. The parent chromene (i.e., 2,2-diphenyl-2H-1benzopyran) without any benzo-annulation or other modifications is known to exhibit photochromism only at very low temperatures (173–263 K).<sup>[4,5]</sup> Indeed, reversion of the open forms to the closed forms in simple benzopyrans is too fast to allow detection of the photogenerated guinonoid intermediates at room temperature. Modulation of the spectrokinetic properties of o-quinonoid intermediates and the associated photochromic phenomenon has been a subject of extensive investigations.<sup>[6]</sup>

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Our own interest has been focused on the photochromism exhibited by chromenes and on modulation of the spectrokinetic properties of the photogenerated colored intermediates derived from chromenes.<sup>[7]</sup> As mentioned earlier, aromatic annulation,<sup>[7a]</sup> electronic effects transmitted by arylation<sup>[7b-7d]</sup> and fluorenylation,<sup>[8]</sup> toroidal conjugation extant to the systems based on hexaphenylbenzenes,<sup>[7e]</sup> etc. have been shown to influence the photochromic phenomenon of chromenes. We recently showed that helicity, as a steric force, allows unprecedented stabilization of the otherwise fleeting photogenerated colored *o*-quinonoid intermediates.<sup>[7h]</sup> The influence of through-space electronic effects has also been demonstrated in chromenes with cofacially oriented aryl rings<sup>[7f]</sup> and also in paracyclophanes grafted with chromenes.<sup>[7g,7i]</sup> Compelling evidence has emerged from our studies that strong mesomeric effects influence the spectral as well as kinetic behavior of the photogenerated colored o-quinonoid intermediates to permit their observation at room temperature. In a continuation of these investigations, we were motivated to examine how arylethynylation of chromenes modifies spectral attributes as well as stabilization of the photogenerated colored o-quinonoid intermediates. Unlike in arylchromenes, the ethynyl spacer should be expected to completely offset steric inhibition of resonance in addition to bringing about a bathochromic shift of the absorptions of the photogenerated colored intermediates. We, therefore, designed and synthesized 5-/6-/7-phenylethynylchromenes (5-/6-/7-PhE) and their diphenylamino-functionalized analogues, 5-/6-/7-(N,N-diphenylamino)phenylethynylchromenes (5-/6-/7-DpaPhE; Figure 1), to explore the phenomenon of photochromism.

Herein, we report that simple phenyl/arylethynylation of the parent chromene brings about remarkable stabilization of photogenerated colored intermediates to the extent that their

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Figure 1. Molecular structures of the aryl- and arylethynylchromenes.

thermal bleaching kinetics approach those observed for commercially relevant naphthopyrans.

### **Results and Discussion**

#### Synthesis of Arylethynyl-Substituted Chromenes

The synthesis of target chromenes 5-/6-/7-PhE and 5-/6-/7-Dpa-PhE, is shown in Scheme 1. To begin with, 3-/4-iodophenol was annulated with 1,1-diphenylpropargyl alcohol following the conventional Claisen rearrangement route using *p*-toluenesulfonic acid (PTSA) as a catalyst. The resultant 5-/6-/7-iodochromenes were subjected to Sonogashira/"sila"-Sonogashira cross-coupling reactions<sup>[9]</sup> under Pd<sup>0</sup>-catalyzed conditions to afford the target chromenes in excellent isolated yields (Scheme 1).

#### Spectrokinetic Properties of the Photochromic Arylethynyl-Substituted Chromenes

The absorption spectra of all phenyl/arylethynyl-substituted chromenes 5-/6-/7-PhE and 5-/6-/7-DpaPhE in toluene



Scheme 1. Synthesis of arylethynylchromenes.





Table 1.	Absorption	properties and	spectrokinetic	data of chromene	es and their respectiv	e photogenerated	colored intermediates.

Chromene	Absorption properties <sup>[a,b]</sup>		Decay rates [s <sup>-1</sup> ] <sup>[c]</sup>	
	Before <i>h</i> ν [nm] (ε)	After <i>h</i> v [nm]	<i>k</i> <sub>1</sub>	k <sub>2</sub>
2H-Chromene <sup>[d]</sup>	310	410, 510 <sup>[e]</sup>	[f]	
5-Ph <sup>[g]</sup>	317 (br, 4026)	416 (br)	[h]	
6-Ph <sup>[g]</sup>	322 (br, 2669)	414 (br), 522 (br)	0.06	0.002
7-Ph <sup>[g]</sup>	325 (12740)	422, 530 (sh)	0.14	0.002
5-DpaPh <sup>[g]</sup>	313 (28435)	484	[h]	
6-DpaPh <sup>[g]</sup>	322 (39944)	424, 564 (br)	0.07	0.011
7-DpaPh <sup>[g]</sup>	355 (33237)	474	0.11	0.008
5-PhE	300 (br, 25965)	422 (br)	[h]	
6-PhE	302 (br, 28525)	421 (br), 545 (br)	0.014 (76)	0.005 (24)
7-PhE	310 (36550)	440	0.023 (99)	0.006 (1)
5-DpaPhE	360 (30640)	488 (br)	[h]	
6-DpaPhE	350 (42390)	424, 577 (br)	0.013 (75)	0.005 (25)
7-DpaPhE	364 (46285)	497	0.021 (99)	0.006 (1)

[a] Based on absorption spectra of phenyl/arylethynyl-substituted chromenes in toluene solutions  $(4 \times 10^{-5} \text{ m})$ . [b] br: broad and sh: shoulder. [c] Unless otherwise mentioned, the decays for the photogenerated colored intermediates were monitored at 288 K after steady-state irradiation for 3–5 min. The amplitudes (%) of the fast  $(k_1)$  and slow  $(k_2)$  decaying components are shown in the parenthesis. [d] Based on absorption spectra of 2,2-diphenyl-2*H*-1-benzopyran in ethanol at 295 K, see ref.<sup>[5]</sup> [e] Obtained from microsecond laser flash experiments using a Q-switched Nd-YAG laser with excitation at 266 nm, see ref.<sup>[5]</sup> The absorption band at 410 nm is the strong band. [f] The lifetime of the colored species is in the microsecond time scale, see ref.<sup>[5]</sup> [g] From ref.<sup>[7b]</sup> at 288 K. [h] The decay was too fast to allow monitoring.

 $(4 \times 10^{-5} \text{ M})$  are shown in Figure 2. The long-wavelength absorption maximum ( $\lambda_{max}$ ) and the molar extinction coefficient ( $\varepsilon$ ) at  $\lambda_{max}$  for each case are collected in Table 1. Analysis of the spectra reveals that the absorptions corresponding to  $\pi,\pi^*$  transitions taper off well below 390 and 425 nm for PhE and DpaPhE series, respectively. As evident from Figure 2, the spectral attributes are different for the differently-substituted analogues of chromenes. The absorptions of 7-arylethynyl-substituted chromenes are considerably redshifted when compared with those of the 5-/6-substituted analogues.



Figure 2. UV/Vis absorption spectra of 5-/6-/7-PhE (a) and 5-/6-/7-DpaPhE (b) in toluene (4  $\times$  10<sup>-5</sup> m).

As shown in Table 1, the phenyl/arylethynyl-substituted chromenes 5-/6-/7-PhE and 5-/6-/7-DpaPhE are found to exhibit remarkably higher molar extinction coefficients when compared with those of the corresponding aryl-substituted chromene analogues 5-/6-/7-Ph and 5-/6-/7-DpaPh. Furthermore, the diphenylaminophenylethynyl-substituted chromenes 5-/6-/7-DpaPhE exhibit significantly redshifted absorption maxima (ca. 50 nm) and considerably higher molar extinction coefficients when compared with those of phenylethynyl-substituted analogues 5-/6-/7-PhE.

Their photochemical behavior was examined in toluene (ca.  $2 \times 10^{-3}$  M as well as  $5 \times 10^{-4}$  M) at 288 K (see the Supporting Information). Upon exposure to UV irradiation ( $\lambda_{ex}$  ca. 350 nm), the colorless solutions of the chromenes were found to undergo ready coloration, which varied from orange-yellow to

blue. The UV/Vis absorption spectra of all chromenes before and after photoirradiation are shown in Figure 3 and in the Supporting Information. Whereas photoirradiation of 6-PhE led to purple-violet coloration with absorption maximum at ca. 545 nm, that of 6-DpaPhE led to dark-blue coloration with  $\lambda_{max}$ at ca. 577 nm (Table 1). In stark contrast, irradiation of 5- and 7-substituted chromenes 5-PhE/5-DpaPhE and 7-PhE/7-DpaPhE, led to yellow ( $\lambda_{max} = 422/488$  nm) and orange-red coloration ( $\lambda_{max} = 440/497$  nm), respectively. It is noteworthy that the colored photogenerated intermediates derived from 6-phenyl/arylethynyl-substituted chromenes displayed highly redshifted absorptions (ca. 80–105 nm) as compared with those of the species derived from the corresponding 5- and 7-substituted regioisomers (Table 1). Furthermore, among the differently substituted chromenes, 7-phenyl/arylethynyl-substituted derivatives



Figure 3. UV/Vis absorption spectra (ca.  $2 \times 10^{-3}$  m in toluene) of 6-PhE (a), 7-PhE (b), 6-DpaPhE (c) and 7-DpaPhE (d) before (black) and after photoirradiation (red). Note the changes in the colors of the solutions after steady-state photoirradiation.





were found to exhibit better colorability (see the Supporting Information).

The photogenerated colored intermediates of phenyl/arylethynyl-substituted chromenes were found to revert to the colorless forms within 2-3 min on standing in the dark at room temperature. The thermal decay kinetics of the colored species, with the exception of those of 5-phenyl/arylethynyl-substituted chromenes, were followed by monitoring changes in the absorbance with time at their respective long-wavelength absorption maxima; the thermal reversion of the colored intermediates of 5-phenyl/arylethynyl-substituted chromenes was found to be too fast to allow their decay kinetics to be monitored at 288 K. Thus, solutions of the chromenes in toluene were exposed to UV radiation until the photostationary state (PSS) was reached. Subsequently, the change in the absorbance at the absorption maximum of the colored intermediate with time was followed at 288 K for each case (Figure 4). The duration of irradiation for attainment of the PSS was determined from a coloration plot in each case (see the Supporting Information).



Figure 4. Comparative normalized thermal decay profiles of the photogenerated colored intermediates of 6-/7-PhE (a) and 6-/7-DpaPhE (b) in toluene at 288 K. The wavelengths at which the decays were monitored are given in parentheses.

The decay in each case was best fitted to a biexponential function (Table 1). Comparison of the data shows that faster thermal decays are observed for the colored intermediates of 7-PhE ( $k_1 = 0.023 \text{ s}^{-1}$ ) and 7-DpaPhE ( $k_1 = 0.021 \text{ s}^{-1}$ ) when com-

pared with those of 6-PhE ( $k_1 = 0.014 \text{ s}^{-1}$ ) and 6-DpaPhE ( $k_1 = 0.013 \text{ s}^{-1}$ ). Remarkably slower rates of decay (ca. 4–6 times) are observed for 6-/7-PhE and 6-/7-DpaPhE when compared with those of the arylchromene analogues 6-/7-Ph and 6-/7-DpaPh. This attests to the considerable influence of the ethynyl spacer on the spectrokinetic properties of the photogenerated colored intermediates. Furthermore, coloration-reversion cycles for two representative chromenes, namely, 6- and 7-DpaPhE, which were carried out to examine their stabilities, did not reveal any indication of degradation,<sup>[10]</sup> which attests to their respectable stabilities upon photoirradiation.

# Influence of the Ethynyl Spacer on the Photochromic Behavior

Mechanistic details of the photochromism of chromenes have been extensively investigated.<sup>[6]</sup> Suffice it to say that the TC and TT isomers shown in Scheme 2 are mainly responsible for the observed coloration upon UV irradiation of chromenes, which results in heterolysis of the C(sp<sup>3</sup>)–O bond in the singlet excited state. The TT isomer is generated by a two-photon absorption of the chromene through initial formation of the TC isomer. Due to the requirement of two-photon absorption, the TT isomer is likely to be formed only minimally when the chromene is subjected to UV irradiation for short durations. Thus, at shorter durations of irradiation, it is the TC isomer that is largely responsible for the observed color.<sup>[11]</sup> The parent chromene, i.e., 2,2diphenyl-2H-1-benzopyran, is known to exhibit photochromism only at low temperatures (173-263 K).<sup>[4,5]</sup> Reversion of the oquinonoid intermediates (open forms) to the precursor closed form occurs too rapidly to allow detection of the former at room temperature.

Our primary objective in investigating the photochromic behavior of arylethynyl-substituted chromenes was to establish the extent to which the ethynyl spacer mediates  $\pi$ -conjugation between phenyl/aryl and benzopyran rings, and modifies absorption as well as the lifetimes of the *o*-quinonoid intermediates generated by photoexcitation. Of the three substituted



(colored *transoid* o-quinonoids)

Scheme 2. Mechanistic paradigm for the photochromism of 2H-chromene.

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chromenes, weak photochromism was generally observed with 5-substituted derivatives in the sense that the photogenerated colored species revert too rapidly; electronic effects are transmitted poorly at this position, whereas the steric bulk preclude mesomeric effects.<sup>[7b,7d]</sup> We shall, therefore, limit ourselves to the photochromic phenomenon observed with 6- and 7-substituted chromenes. The fact that strong mesomeric effects are operative between the phenyl/arylethynyl moiety and the benzene ring of the benzopyran is evident from the shifts in the absorptions of the closed as well as open forms generated upon photolysis. As far as phenylethynylchromenes are concerned, the mesomeric effect is manifested in hypsochromic shifts of the shorter wavelength absorption maxima and very high molar absorptivities relative to those of 6- and 7-phenylchromenes. In contrast, bathochromic shifts are observed in the absorption maxima of their corresponding photogenerated oquinonoid intermediates. Highly pronounced effects are observed for 6- and 7-diphenylaminophenylethynyl-substituted chromenes. Bathochromic shifts of 9-28 nm are observed for the absorptions of the closed forms and 13-23 nm for absorption of the ring-opened forms, relative to the corresponding diphenylaminophenyl-substituted chromenes (Table 1). Here also, the molar absorptivities are almost double for the closed forms, attesting to the transmission of the effect due to the electron-releasing diphenylamino substituent. The positional dependence of the absorption maximum, particularly for the photogenerated o-quinonoid intermediates, is noteworthy; a more redshifted absorption is observed for functionalization at the 6-position compared with that for functionalization at the 7-position for a given substituent. This shift is as much as 105 nm for 6-/7-PhEs and 80 nm for 6-/7-DpaPhEs. Furthermore, the introduction of C=C between the phenyl and diphenylbenzopyran as in 6-/7-PhEs brings about a bathochromic shift in the absorptions of the colored intermediates by 18-23 nm, when compared with those of 6-/7-Phs. Likewise, a bathochromic shift of ca. 13–23 nm is observed for the absorption of colored intermediates of 6-/7-DpaPhEs when compared to those of 6-/7-DpaPhs. Clearly, the mesomeric effects operate differently and significantly for the chromenes functionalized with phenyl/arylethynyl groups.

The thermal reversion kinetics followed in each case by monitoring change in the absorbance of the colored intermediate at long wavelength absorption maximum show remarkable increase in the lifetimes (1/k) of the colored *o*-quinonoid intermediates, as revealed by the decay rate constants  $k_1$  and  $k_2$ . In general, the fast-decaying component, i.e.,  $k_1$ , is predominant and is largely responsible for the observed color. As mentioned earlier, this component is attributed to the TC isomer (Scheme 2), whereas  $k_2$  is attributed to the minor TT isomer, which is generated by two-photon absorption; the latter may be assumed to be unimportant for spectrokinetic analyses. Thus, the o-quinonoid intermediates of 6-PhE and 6-DpaPhE are found to decay ca. 4-fold slower relative to those of 6-Ph and 6-DpaPh. Likewise, the colored species of 7-PhE and 7-DpaPhE are found to decay ca. 5-fold slower than those of 7-Ph and 7-DpaPh; the decay rates of the o-quinonoid intermediates of 6-PhE and 6-DpaPhE are similar to those of 7-PhE and 7-DpaPhE. For the two different substitutions, i.e., at the 6- and 7-positions, the colored species in the case of 6-phenyl/arylethynylchromenes are found to decay ca. 1.5-fold slower than those of 7phenyl/arylethynylchromenes. It turns out that the observed spectrokinetic properties of 6-/7-phenyl/arylethynyl chromenes are remarkably better than those of a large number of photochromic chromenes reported to date. In fact, the stabilities of the photogenerated colored intermediates due to phenyl/arylethynylation are much higher than those achieved with heterocyclic substitution,<sup>[6a]</sup> hetero-fusion,<sup>[8]</sup> aromatic annulation,<sup>[7a]</sup> toroidal conjugation,<sup>[7e]</sup> or complexation with metal ions,<sup>[2d]</sup> etc. The decay rate constants at room temperature for the photogenerated colored intermediates of some of the commercially



Figure 5. Structures of some commercially relevant and well-known naphthopyrans. Thermal decay rate constants at room temperature for their photogenerated colored intermediates are given in parentheses.

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Scheme 3. Mesomeric effects in 6-/7-DpaPhEs and their respective o-quinonoid intermediates.

relevant and well-known naphthopyrans, namely, 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (NP1, also known as *Reversacol Rush Yellow*),<sup>[12a,12b]</sup> 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran (NP2),<sup>[12a]</sup> 2,2-bis(4-methoxyphenyl)-5,6-dimethyl-2*H*-naphtho[1,2-*b*]pyran (NP3, also known as *Reversacol Berry Red*),<sup>[12c]</sup> 2-(4'-piperidinophenyl)-2-phenyl-5-methoxycarbonyl-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran (NP4),<sup>[12d]</sup> and 2-(4'-dimethylaminophenyl)-2-(4''-methoxyphenyl)-5-hydroxymethyl-9-pyrrolidino-2*H*-naphtho[1,2-*b*]-pyran (NP5)<sup>[12d]</sup> are shown in Figure 5. The data presented in Table 1 show that the colored intermediates of arylethynylchromenes exhibit bleaching rate constants much better than those of NP1/NP4/NP5 and approach those of NP3, namely, *Reversacol Berry Red*.

The remarkable changes in the spectrokinetic properties of the photogenerated colored o-quinonoid intermediates can be understood from the resonating structures shown in Scheme 3. Accordingly, more extended mesomeric effect in the case of 7substituted chromene than in the 6-substituted analogue should account for the observed redshift in the absorption maximum of the former. In a similar manner, the differences in the absorption behaviors of the photogenerated quinonoid species can also be traced to differences in their mesomeric structures. One observes an extended conjugation in the case of the o-quinonoid intermediate of 6-DpaPhE, whereas the conjugation is truncated in the case of the intermediate of 7-Dpa-PhE. In essence, the absorption maximum in the case of chromene 6-DpaPhE is blueshifted compared with that of 7-DpaPhE, but the former gives rise to guinonoid intermediates with more extended conjugation. The fact that the extended conjugation is manifested in more stabilization is clearly borne out from slower decay kinetics of the colored species in the case of 6phenyl/arylethynylchromenes as compared with those of 7phenyl/arylethynylchromenes. The noteworthy feature of the ethynyl spacer is that the conjugation between two aryl rings at the termini is freely facilitated without any sterically imposed constraints because of the cynlidrical electronic distribution.

## Conclusions

It is shown that simple phenyl/arylethynyl-substituted chromenes can be readily accessed by Sonogashira/"sila"-Sonogashira coupling as a key reaction. Photoirradiation of all the arylethynylchromenes leads to readily observable color changes at room temperature, with the color observed in the case of 5and 7-substituted chromenes being yellow to orange-red and that in the case of 6-substituted analogues being purple-violet to dark-blue. Clearly, functionalization at the 5-, 6-, and 7-positions results in varying degrees of mesomeric effects, which allow modulation of the absorption properties of chromenes and, more importantly, their photogenerated o-quinonoid intermediates; the colored intermediates of 5-substituted chromenes are found to be too short lived to allow their reversion kinetics to be followed. In contrast, the intermediates of 6- and 7-arylethynyl chromenes are found to be considerably longer lived than those derived from analogous phenyl/aryl-substituted chromenes. Indeed, the spectrokinetic properties of 6-/7phenyl/arylethynyl chromenes are much better than many photochromic chromenes reported to date. The observed results are remarkable in view of the fact that simple phenyl/arylethynylation of halo-substituted chromenes allows access to a series of photochromic systems with tunable spectrokinetic properties at ambient temperatures. Clearly, the resonance effects of





varying magnitudes are nicely relayed through the ethynyl group from one end of the molecular system to the other, without any steric inhibition of resonance, permitting thermal reversion kinetics that are comparable to the intermediates of the commercially relevant naphthopyrans.

## **Experimental Section**

**General Aspects:** Anhydrous tetrahydrofuran (THF) was freshly distilled from sodium prior to use. All other solvents also were distilled prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a JEOL (400 MHz and 100 MHz, respectively) spectrometer in CDCl<sub>3</sub> as solvent. IR spectra were recorded with a Bruker Vector 22 FTIR spectrophotometer. The El mass spectra were recorded with a Waters GCT Premier <sup>Q</sup>TOF machine. Melting points were determined with a JSGW melting-point apparatus. UV/Vis absorption spectra were recorded with a SHIMADZU UV-1800 spectrophotometer. Photolysis was carried out in a Luzchem photoreactor fitted with 350 nm UV lamps (8 W, 14 lamps).

**Synthesis of Precursor 5-/6-/7-lodochromenes:** The precursor 5-/ 6-/7-iodochromenes were prepared by acid-catalyzed condensation reaction between 3-/4-iodophenol and 1,1-diphenylpropargyl alcohol and subsequent Claisen rearrangement. A representative procedure for the synthesis of the iodochromenes is described below.

A 50 mL two-necked, round-bottom flask was charged with 3-/4iodophenol (0.50 g, 2.26 mmol), 1,1-diphenylprop-2-yn-1-ol (0.57 g, 2.72 mmol), a catalytic amount of p-toluenesulfonic acid (0.04 mg, 0.22 mmol), and anhydrous CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The solution was stirred at room temperature under nitrogen gas atmosphere for 4 h, then washed with saturated Na<sub>2</sub>CO<sub>3</sub> solution, and the mixture was extracted with  $CH_2CI_2$  (3 × 20 mL). The combined extract was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to dryness under reduced pressure. Further purification of the crude material by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 8 %) afforded the iodochromene either as a colorless crystalline material or as a viscous liquid in a respectable yield (65-68 %). Whereas 4-iodophenol yielded exclusively 6-iodochromene as a colorless crystalline material (0.61 g, 65 %), 3-iodophenol led to an inseparable mixture (colorless viscous liquid, 0.63 g, 68 %) of regioisomers, i.e., 5- and 7iodochromenes, in 1:1.8 ratio. The regioisomeric mixture was used as such for the next step without further separation.

**6-Iodo-2,2-diphenyl-2H-1-benzopyran:** Colorless crystalline solid; m.p. 134–136 °C. IR (KBr):  $\tilde{v} = 3049$ , 3028, 1631, 1595, 1489, 1472, 1244, 1213, 1128 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 6.20$  (d, J = 10.0 Hz, 1 H), 6.55 (d, J = 10.0 Hz, 1 H), 6.70 (d, J = 8.7 Hz, 1 H), 7.27 (d, J = 3.2 Hz, 1 H), 7.29–7.36 (m, 6 H), 7.38–7.42 (m, 5 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 83.1$ , 118.8, 122.1, 123.5, 126.9, 127.7, 128.2, 129.9, 134.9, 138.0, 144.4, 152.4 ppm. MS (EI<sup>+</sup>): *m/z* calcd. for C<sub>21</sub>H<sub>15</sub>OI [M]<sup>+</sup> 410.0168; found 410.0168.

**Synthesis of Phenylethynylchromenes (5-/6-/7-PhE):** These compounds were synthesized by Sonogashira coupling reaction of iodochromenes under Pd<sup>0</sup>-catalyzed conditions. A representative procedure for the synthesis of 6-PhE is described below.

Into a two-necked, round-bottom flask charged with 6-iodo-2,2-diphenyl-2*H*-1-benzopyran (0.50 g, 1.22 mmol), phenylacetylene (0.20 mL, 1.83 mmol), THF (20 mL), and triethylamine (10 mL), were introduced Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.09 g, 0.12 mmol) and Cul (0.03 g, 0.18 mmol). The resultant reaction mixture was stirred at room temperature under nitrogen gas atmosphere for 5 h. Upon completion of the reaction as judged by TLC analysis, the reaction mixture was concentrated to dryness in vacuo. The crude material was dissolved in  $CH_2Cl_2$  (30 mL), washed with brine solution, and the organic contents were extracted with  $CH_2Cl_2$  (3 × 20 mL). The combined extract was dried with anhydrous  $Na_2SO_4$ , filtered, and concentrated to dryness under reduced pressure. The crude material was subjected to silica gel column chromatography ( $CH_2Cl_2$ /hexane, 10 %) to afford pure 6-(phenylethynyl)-2,2-diphenyl-2*H*-1-benzopyran (0.42 g, 89 %) as a colorless solid.

**6-(Phenylethynyl)-2,2-diphenyl-2***H***-1-benzopyran (6PhE):** Colorless crystalline solid; m.p. 150–152 °C. IR (KBr):  $\ddot{v}$  = 3051, 2921, 2201, 1630, 1595, 1492, 1480, 1445, 1364, 1270, 1246, 1117 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.21 (d, *J* = 10.0 Hz, 1 H), 6.61 (d, *J* = 10.0 Hz, 1 H), 6.90 (d, *J* = 8.7 Hz, 1 H), 7.21 (d, *J* = 1.4 Hz, 1 H), 7.26–7.30 (m, 3 H), 7.31–7.36 (m, 7 H), 7.41–7.44 (m, 4 H), 7.46–7.51 (m, 2 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 83.1, 88.0, 89.2, 115.9, 116.7, 121.1, 122.8, 123.5, 126.9, 127.6, 127.9, 128.2, 128.3, 129.5, 129.8, 131.4, 133.0, 144.5, 152.7 ppm. MS (EI<sup>+</sup>): *m/z* calcd. for C<sub>29</sub>H<sub>20</sub>O [M]<sup>+</sup> 384.1514; found 384.1514.

The Sonogashira coupling reaction of a mixture of 5- and 7-iodo-2,2-diphenyl-2*H*-1-benzopyran (0.5 g) with phenylacetylene as described above led to a mixture of 5- and 7-(phenylethynyl)-2,2-diphenyl-2*H*-1-benzopyrans (0.398 g, 85%). The two regioisomeric chromenes were separated by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 5%).

**7-(Phenylethynyl)-2,2-diphenyl-2H-1-benzopyran (7-PhE):** Yield 0.257 g (55 %); colorless crystalline solid; m.p. 118–120 °C. IR (KBr):  $\tilde{v}$  = 3056, 2923, 2852, 2210, 1635, 1607, 1540, 1500, 1447, 1324, 1255, 1214, 1107 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.20 (d, *J* = 10.0 Hz, 1 H), 6.61 (d, *J* = 10.0 Hz, 1 H), 6.97 (d, *J* = 7.8 Hz, 1 H), 7.02 (dd, *J* = 7.8, 1.3 Hz, 1 H), 7.10 (s, 1 H), 7.24–7.29 (m, 2 H), 7.30–7.36 (m, 7 H), 7.41–7.45 (m, 4 H), 7.49–7.53 (m, 2 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 82.7, 89.4, 89.8, 119.4, 121.4, 122.9, 123.2, 124.0, 124.8, 126.4, 126.9, 127.5, 128.1, 128.2, 128.3, 129.7, 131.6, 144.6, 152.2 ppm. MS (El<sup>+</sup>): *m/z* calcd. for C<sub>29</sub>H<sub>20</sub>O [M]<sup>+</sup> 384.1514; found 384.1516.

**5-(Phenylethynyl)-2,2-diphenyl-2***H***-1-benzopyran (5-PhE):** Yield 0.141 g (30 %); colorless viscous liquid. IR (KBr):  $\tilde{v} = 3056$ , 2930, 2850, 2215, 1635, 1607, 1540, 1488, 1417, 1324, 1256, 1214, 1107 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 6.28$  (d, J = 10.0 Hz, 1 H), 6.93 (d, J = 10.0 Hz, 1 H), 7.05 (m, 2 H), 7.15 (d, J = 10.0 Hz, 1 H), 7.26–7.30 (m, 2 H), 7.32–7.39 (m, 7 H), 7.43–7.47 (m, 4 H), 7.54–7.57 (m, 2 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 82.5$ , 86.7, 93.6, 116.9, 120.2, 121.5, 122.4, 123.1, 124.9, 127.0, 127.5, 128.1, 128.4, 129.0, 129.7, 131.6, 144.6, 152.4 ppm. MS (El<sup>+</sup>): *m/z* calcd. for C<sub>29</sub>H<sub>20</sub>O [M]<sup>+</sup> 384.1514; found 384.1514.

**Synthesis of 4-Diphenylaminophenylethynylchromenes (5-/6-/ 7-DpaPhE):** These compounds were synthesized by "sila"-Sonogashira coupling reaction of the precursor iodochromenes under Pd<sup>0</sup>catalyzed conditions. A representative procedure is described for the synthesis of 6-DpaPhE.

To a two-necked, round-bottom flask (50 mL) charged with 6-iodo-2,2-diphenyl-2*H*-1-benzopyran (0.60 g, 1.46 mmol), *N*,*N*-diphenyl-4-[(trimethylsilyl)ethynyl]aniline (1.0 g, 2.92 mmol), THF (20 mL), and triethylamine (10 mL) were added tetrabutylammonium fluoride trihydrate (1.84 g, 5.84 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.10 g, 0.14 mmol), and Cul (0.04 g, 0.22 mmol). The reaction mixture was stirred under nitrogen gas atmosphere at 60 °C for 6 h. Upon completion of the reaction as judged by TLC analysis, the reaction mixture was concentrated to dryness under reduced pressure. The crude material was subsequently dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL), washed with brine, and the organic matter was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The combined extract was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and



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concentrated to dryness under reduced pressure. The crude residue was subjected to silica gel column chromatography ( $CH_2CI_2$ /hexane, 10 %) to give pure 6-(4-diphenylaminophenylethynyl)-2,2-diphenyl-2*H*-1-benzopyran (0.68 g, 84 %) as a light-yellow crystalline solid.

**6-(4-Diphenylaminophenylethynyl)-2,2-diphenyl-2H-1-benzopyran (6-DpaPhE):** Light-yellow crystalline solid; m.p. 130–132 °C. IR (KBr):  $\ddot{v}$  = 3034, 2923, 2204, 1634, 1587, 1507, 1485, 1331, 1282, 1242, 1128 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.19 (d, *J* = 10.0 Hz, 1 H), 6.59 (d, *J* = 10.0 Hz, 1 H), 6.88 (d, *J* = 8.2 Hz, 1 H), 6.96–7.00 (m, 2 H), 7.02–7.12 (m, 6 H), 7.17 (s, 1 H), 7.21–7.28 (m, 7 H), 7.29–7.35 (m, 6 H), 7.39–7.43 (m, 4 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 83.0, 88.2, 88.4, 116.2, 116.5, 116.7, 121.0, 122.5, 122.8, 123.4, 124.8, 127.0, 127.6, 128.1, 129.3, 129.4, 129.6, 132.3, 132.8, 144.5, 147.2, 147.6, 152.5 ppm. MS (El<sup>+</sup>): *m/z* calcd. for C<sub>41</sub>H<sub>29</sub>NO [M]<sup>+</sup> 551.2249; found 551.2244.

A similar "sila"-Sonogashira coupling reaction of a mixture of 5- and 7-iodo-2,2-diphenyl-2H-1-benzopyran (0.6 g) with *N*,*N*-diphenyl-4-[(trimethylsilyl)ethynyl]aniline as described above gave rise to a mixture of 5- and 7-(4-diphenylaminophenylethynyl)-2,2-diphenyl-2H-1-benzopyrans (0.71 g, 88 %). The two regioisomeric chromenes were separated by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 5 %).

**7-(4-Diphenylaminophenylethynyl)-2,2-diphenyl-2H-1-benzopyran (7-DpaPhE):** Yield 0.46 g (57 %); light-yellow crystalline solid; m.p. 158–160 °C. IR (KBr):  $\tilde{v} = 3032$ , 2924, 2203, 1635, 1585, 1510, 1489, 1446, 1331, 1278, 1217, 1108 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 6.19$  (d, J = 10.0 Hz, 1 H), 6.61 (d, J = 10.0 Hz, 1 H), 6.90–7.02 (m, 4 H), 7.03–7.08 (m, 3 H), 7.09–7.14 (m, 4 H), 7.23–7.29 (m, 6 H), 7.30–7.37 (m, 6 H), 7.40–7.45 (m, 4 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 82.7$ , 88.7, 90.2, 116.0, 119.2, 121.1, 122.2, 122.9, 123.5, 124.4, 124.6, 124.9, 126.4, 126.9, 127.5, 128.1, 129.3, 129.4, 132.5, 144.7, 147.1, 147.9, 152.2 ppm. MS (EI<sup>+</sup>): *m/z* calcd. for C<sub>41</sub>H<sub>29</sub>NO [M]<sup>+</sup> 551.2249; found 551.2247.

**5-(4-Diphenylaminophenylethynyl)-2,2-diphenyl-2H-1-benzopyran (5-DpaPhE):** Yield 0.251 g (31 %); light-yellow viscous liquid. IR (KBr):  $\ddot{v}$  = 3033, 2920, 2203, 1635, 1586, 1509, 1489, 1331, 1278, 1218, 1108 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.24 (d, *J* = 10.0 Hz, 1 H), 6.89 (d, *J* = 10.0 Hz, 1 H), 6.98–7.03 (m, 3 H), 7.04–7.09 (m, 3 H), 7.10–7.15 (m, 5 H), 7.24–7.29 (m, 6 H), 7.30–7.39 (m, 6 H), 7.41–7.45 (m, 4 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 82.5, 86.0, 93.9, 115.9, 116.6, 120.6, 121.6, 122.2, 123.0, 123.6, 124.8, 124.9, 127.0, 127.5, 128.1, 128.9, 129.4, 129.5, 132.5, 144.7, 147.1, 148.0, 152.4 ppm. MS (El<sup>+</sup>): *m/z* calcd. for C<sub>41</sub>H<sub>29</sub>NO [M]<sup>+</sup> 551.2249; found 551.2247.

**Supporting Information:** Synthesis of starting materials, solutionstate photolyses of arylethynylchromenes, coloration plots, photostability of the arylethynylchromenes and <sup>1</sup>H and <sup>13</sup>C NMR spectra of all the compounds.

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