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Through-Space Control of the Persistence of Photogenerated *o*-Quinonoid Intermediates in Naphthalenes Containing Cofacially Oriented Chromenes and Arenes[‡]

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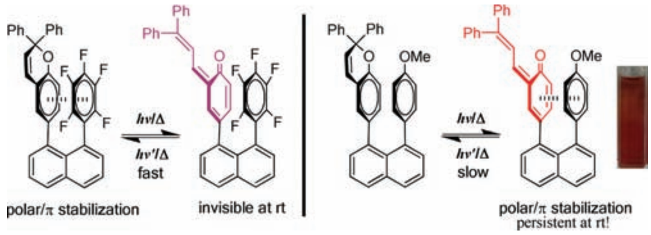
ABSTRACT



Remarkable modulation of the persistence of the photogenerated colored *o*-quinonoid intermediates via a through-*space* interaction has been demonstrated in chromenes 1–4 based on 1,8-diarylnaphthalenes. Polar/π interaction is shown to stabilize the closed form of 4 to such an extent that photoinduced coloration is virtually invisible, while the same stabilization in the opened form of 2 permits ready coloration with a long-lived *o*-quinonoid intermediate.

Molecule-based electronic materials are relevant in miniaturized hybrid devices that can perform magnification, rectification, and switching operations similar to those exhibited by microscopic silicon-based analogs. In particular, photoresponsive materials are of significant importance from the point of view of their applications in variable transmission glasses, nanoscale sensors, high density optical data storage, molecular machines, etc.[1−3] Among diverse classes of photochromic compounds, arylchromenes (2*H*-benzopyrans and 2*H*-naphthopyrans) have been extensively investigated in view of their industrial application in ophthalmic lenses.[1c] 2,2-Diarylchromenes readily undergo photoinduced C−O bond heterolysis to ring-opened colored *o*-quinonoid intermediates, which revert back to the closed form (colorless) either by exposing to visible light or by keeping in the dark.[4,5] We have been interested in the modulation of spectrokinetic properties of the colored *o*-quinonoid intermediates;[6] we have shown that simple arylation at 6- and 7-positions of the chromene nucleus can manifest, via mesomeric effects in dramatically distinct absorptions of the intermediates and associated decay kinetics.[6b,d] We have also shown that the helical environment around the chromene moiety also modifies the spectrokinetic properties of the photogenerated

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[‡] Dedicated to Prof. Gautam R. Desiraju on the occasion of his 60th birthday.

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o-quinonoid intermediates.[6a] In our recent investigations, we delineated the effect of electronic coupling via toroidal delocalization on the photochromism of chromenes that are constrained to be part of the hexaphenylbenzene scaffold.[6e] During these investigations, our attention was drawn to the voluminous investigations by Siegel et al.[7] on establishing the nature of interaction between cofacially oriented aryl rings substituted at the 1,8-positions of the naphthalene core. While scant evidence has been offered in favor of the charge-transfer interaction between the aryl rings experimentally,[8] polar/π effect (a through-space Coulombic interaction) has been shown to be responsible for the behavior and stability of 1,8-diarylnaphthalene derivatives. We wondered as to how the nature of interaction, i.e., charge-transfer or polar/π effect, may manifest in the photochemistry of naphthalenes substituted at 1,8-positions with chromene and an aryl ring that contains different substituents. As the chromenes and their photogenerated *o*-quinonoid intermediates are complementary to each other in terms of electronic properties (the former being electron-rich and the latter being electron-poor), the spectrokinetic properties of the intermediates were a priori expected to relay information on the true nature of the interaction. Herein, we report the photochemistry of chromenes based on naphthalenes **1**–**4** that contain cofacially oriented aryl rings and remarkable through-space control of the lifetimes of quinonoid intermediates (Figure 1).

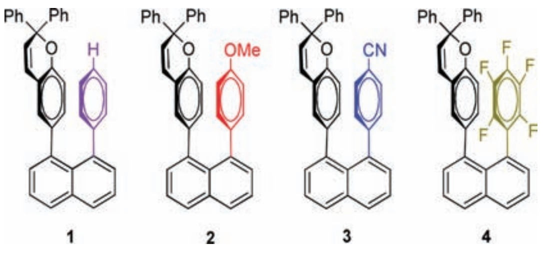
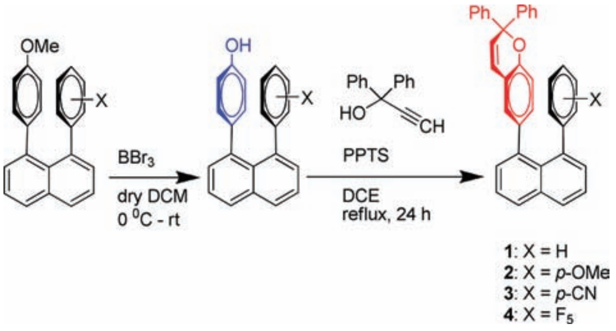


Figure 1. Structures of the chromenes based on naphthalene core.

The naphthalene-based chromenes **1**–**4** were readily synthesized from their precursor 1-(4-hydroxyphenyl)-8-arylnaphthalenes by PPTS (pyridinium-*p*-toluenesulfonate)-mediated cyclocondensation reaction, Scheme 1. The latter were accessed by Pd(0)-catalyzed Suzuki coupling reactions; see the Supporting Information. All chromenes **1**–**4** were thoroughly characterized by IR, ^{1}H NMR, ^{13}C NMR, and ESI-MS spectroscopic analyses.

Scheme 1



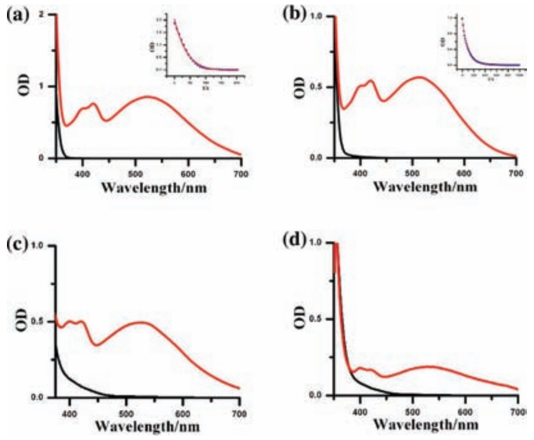


Figure 2. The absorption spectra of chromenes (a) **1**, (b) **2**, (c) **3**, and (d) **4** before (black) and after irradiation (red) in toluene with λ = 350 nm at 298 K (**1** and **2**) and at 278 K (**3** and **4**). The concentrations of the chromenes in toluene were typically 4–5 × 10^{-3} M. Also shown in the insets are decay profiles of the intermediates of **1** and **2**.

Steady-state irradiation of the solutions of chromenes **1** and **2** in toluene (4–5 × 10^{-3} M) contained in 3-cm quartz cuvettes at λ = 350 nm in a photoreactor for a few minutes led to purple-red coloration at 298 K. However, similar color changes were not observed for the solutions of chromenes **3** and **4** unless the irradiation was carried out at 278 K. In Figure 2 are shown the absorption spectra of the solutions before and after irradiation; the spectra for **1** and **2** were recorded at rt, while for **3** and **4**, the spectral acquisition was done at 278 K. Clearly, all the chromenes **1**–**4** lead to photogenerated intermediates for which the differences in absorptions are unexceptional.

One observes that the photogenerated intermediates exhibit uniformly a 2-band pattern between 400 and 440 nm followed by a broad absorption band that spans from 450 to 700 nm (Table 1). While the purple-red color in **1** and **2** was found to disappear in 2–3 min at 298 K, that in the case of **3** and **4** was found to revert to the colorless form too rapidly to preclude spectral monitoring of their decays

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Table 1. Absorption Properties of Arylchromenes **1**−**4** and Kinetic Data of Their Photogenerated *o*-Quinonoid Intermediates in Toluene

	absorption properties		
compound	before $h\nu$ (nm) (ε)	after $h\nu$ $\lambda_{\max}$ (nm)[a]	rate k_1 and k_2 (s^{-1})
1	287 (14370)	420, 524	0.021[b]
2	303 (8150)	420, 514	0.010
3	288 (7490)	420, 529	[c]
4	286 (6945)	417, 537	[c]

[a] The long wavelength absorption maximum corresponds to the broad band. [b] The decay curve was fitted to biexponential function; the rate constant refers to the major component. [c] The very short lifetime of the transient *o*-quinonoid intermediate disallowed kinetic monitoring; see text.

at room temperature. In Figure 2 are also shown (inset) the decay kinetics for the disappearance of the colored species derived from chromenes **1** and **2** (Table 1). Of the two colored intermediates of chromenes **3** and **4**, that of the latter was found to decay too rapidly. Thus, the lifetimes of transient intermediates derived from **1**−**4** were found to follow the order **2** > **1** > **3** > **4**. The data in Table 1 show that the intermediate of **1** decays at least two times faster than that of **2**, while that of **3** is much faster and **4** the fastest.

To gain insights concerning relative dispositions of the aryl rings that are cofacial in each of the chromenes **1**−**4**, we sought to establish their X-ray crystal structures. While the crystals suitable for X-ray investigations were obtained for **1**−**3**, our persistent efforts to grow the crystals of **4** were in vain. In Figure 3 are shown the X-ray determined molecular structures of **1**−**3**. The distance between the two aryl moieties ranges from 3.4 to 3.6 Å. It is also noteworthy that the angles between the planes of the aryl rings and the naphthalene core range between 48 and 66°.

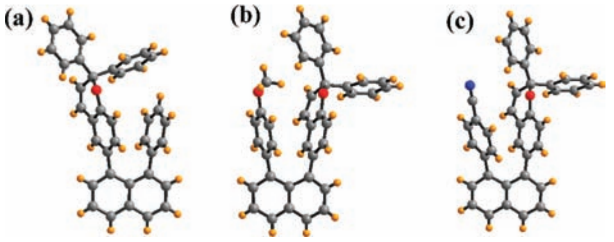
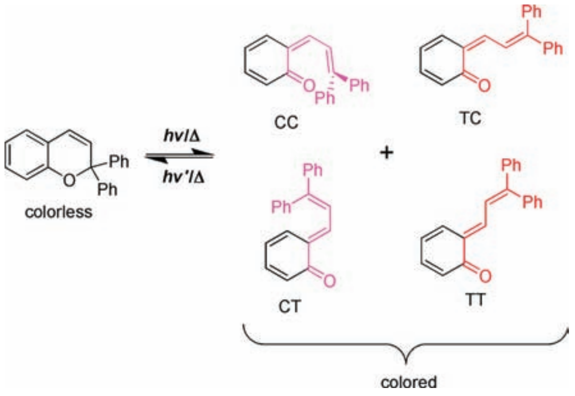


Figure 3. The X-ray determined molecular structures of chromenes (a) **1**, (b) **2**, and (c) **3**.

The photochemistry of chromenes is well established. Accordingly, C−O bond heterolysis in the singlet excited state leads instantaneously to *o*-quinonoid intermediate CC, which may isomerize to TC isomer. Under steady-state irradiation conditions, second photon absorption may populate CT and TT isomers (Scheme 2).[9−12] In general, the CC isomer is known to decay quite rapidly within a few picoseconds.[9−12] It is the TC and TT isomers that are generally observed over a few milliseconds to minutes time scale; the formation of CT is generally ruled out on the basis of steric considerations. Thus, the color that is observed upon photolysis of chromenes is generally attributed to TC and TT isomers; formation of the latter is important only under prolonged durations of irradiation. Otherwise, the species that decays predominantly when chromens are subjected to irradiation for brief periods of irradiation is the TC isomer. The longer-lived TT isomer, formed in small amounts, may interfere with decay kinetics.[6d] In the backdrop of this mechanistic exemplar, let us now consider the spectrokinetic behavior of the photogenerated intermediates of **1**−**4**. As mentioned earlier, the spectral features for all of the intermediates of **1**−**4** are unexceptional. While the colored species attributed to *o*-quinonoid intermediates of **1** and **2** are readily observable at room temperature, those for **3** are barely observable and virtually not for **4**. Furthermore, the fact that the chromene **1** leads to colored intermediates that persist for a few minutes at room temperature is remarkable in light of the fact that the parent chromene, i.e., 2,2-diphenylbenzopyran, does not lend itself to readily observable colored intermediates.[4] It is thus compellingly evident that the substituent(s) in the aryl ring that is cofacially oriented on the naphthalene scaffold with respect to the chromene moiety exert(s) remarkable influence on the behavior of

Scheme 2



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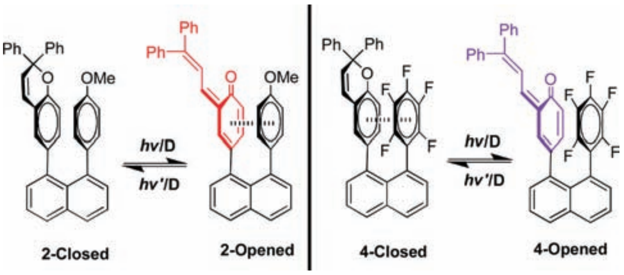
photogenerated *o*-quinonoid intermediates. That the interaction between the aryl ring and the closed chromene/ring-opened *o*-quinonoid moiety can indeed be possible via through-space is evident from the X-ray determined molecular structures of chromenes **1**−**3**. The distance between the centers of the cofacially oriented aryl ring and the benzene ring of the chromene varies between 3.4 and 3.6 Å. This is the distance at which the geometry between two aromatic rings can be effectively stabilized or destabilized or may even lead to reactions, e.g., photodimerizations in the solid state.[13] Although the aryl rings are somewhat tilted with respect to the naphthalene core, their geometries should in principle allow considerable face-to-face overlap.

How does the through-space interaction bring about a dramatic influence on the decay/persistence of the photogenerated *o*-quinonoid intermediates of chromenes based on 1,8-napthalene? A lot of investigation has been carried out to gain insights into the nature of interaction between cofacially oriented arenes. In particular, the emphasis has centered on resolving the dichotomy between electrostatic nature and charge-transfer.[7] It is well-known that the preferred geometry for benzene dimer is slipped/offset parallel geometry in both solution as well as solid state.[14] The interaction between benzenes substituted with electron-donating and electron-withdrawing groups can be understood on the basis of electrostatic force between the quadrupole moments. Indeed, it has been established that the quadrupoles of benzene and hexafluorobenzene are almost equal in magnitude but opposite in sign,[15] so that parallel-stacked geometry is favored for the benzene−hexafluorobenzene dimer. In the case of 1,8-diarylnaphthalenes in which the two aryl rings that are constrained to be cofacial contain electron-donating and electron-withdrawing groups, the interactions can be of two types, i.e., (i) polar (electrostatic and induction) and (ii) van der Waals (dispersion).[7c] As the contact area is small in the case of 1,8-diarylnaphthalenes, the polar term is expected to dominate. The experimental evidence[7] as well as the theoretical calculations[14,15] show that the interaction between the cofacially oriented aryl moieties is polar/π in nature. Further, no strong absorption above 400 nm in the UV−vis absorption spectra has been observed in 1,8-diarylnaphthalenes containing aryl rings that are electronically complementary, which rules out the possibility of charge-transfer.[7] In the present investigation, we did not observe any absorptions that may be attributed to charge-transfer bands in all of the chromenes and their photogenerated intermediates, cf. Figure 2.

To understand the kinetic behavior of *o*-quinonoid intermediates of chromenes **1**−**4**, let us consider **2** and **4**; the former contains an electron-rich arene ring, while the latter an electron-poor ring (Scheme 3). In closed and open forms, the chromene and its photogenerated *o*-quinonoid intermediate should constitute electron-rich and electron-poor rings, respectively. Thus, the polar interaction between the cofacially oriented rings should be stronger in the open form than in the closed form in **2**, while the opposite should hold true in the case of **4**. In other words, the polar/π interaction should stabilize the open form in **2** and destabilize the same in **4**. The behavior of parent chromene **1** and the cyano-substituted derivative **3** should be expected to be within the extremes represented by **2** and **4**. In complete accordance with this reasoning, one observes the persistence of color due to the photogenerated reactive intermediates in the order **2** > **1** > **3** > **4**.

Scheme 3



In summary, remarkable modulation of the persistence of *o*-quinonoid intermediates by through-space interactions has been demonstrated in a variety of chromenes based on 1,8-diarylnaphthalenes. In general, the modulation of kinetic property has been possible via annulation or electronic substituent/mesomeric effects. Through-space control of the kinetic decay of *o*-quinonoid intermediates is heretofore unprecedented, and the results described herein illustrate the finesse with which the behavior of reactive intermediates can be controlled.

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Supporting Information Available. Experimental procedures, spectral data (UV−vis and NMR), spectral reproductions, and crystal structure refinement details. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.