JOC The Journal of Organic Chemistry

ARTICLE

pubs.acs.org/joc

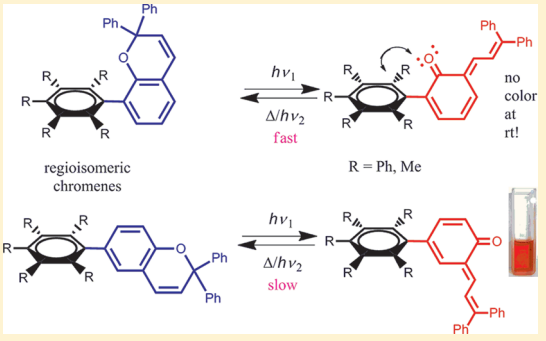
Influence of (2,3,4,5,6-Pentamethyl/phenyl)phenyl Scaffold: Stereoelectronic Control of the Persistence of *o*-Quinonoid Reactive Intermediates of Photochromic Chromenes†

Susovan Mandal, Keshaba Nanda Parida, Subhas Samanta, and Jarugu Narasimha Moorthy*

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

Supporting Information

ABSTRACT: Regioisomeric photochromic chromenes **1**Ch−**6**Ch substituted with the (2,3,4,5,6-pentamethyl/phenyl)phenyl scaffold were designed to delve into stereoelectronic effects on the spectrokinetic properties of photogenerated *o*-quinonoid *reactive* intermediates. While the latter derived from **1**Ch, **2**Ch, **4**Ch, and **5**Ch were found to exhibit notable persistence, those from **3**Ch and **6**Ch were found to revert rapidly at room temperature to preclude visible coloration. The intermediates of **1**Ch and **2**Ch were found to be marginally more stable than those of **4**Ch and **5**Ch, respectively, attesting to the possibility of toroidal conjugation via $C_{ipso}-\pi$ orbitals in the former. The rapid reversion of the intermediates of **3**Ch and **6**Ch is attributed to unfavorable electronic repulsion between the phenyl ring of the (pentamethyl/phenyl)phenyl scaffold and one of the lone-pairs of the *o*-quinonoid oxygen. Thus, the regioisomerically substituted photochromic chromenes are shown to permit control of the reversion, very rapidly as well as slowly, of the colored *o*-quinonoid intermediates through operation of stereoelectronic effects differently.



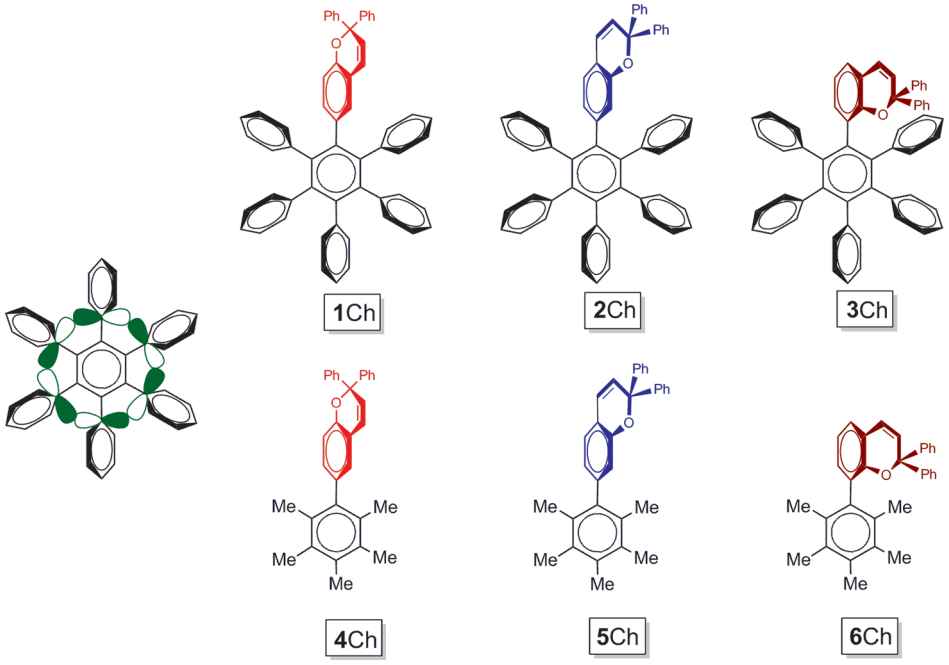
INTRODUCTION

Control of the properties of molecules that respond to external stimuli such as light, heat, H^+, voltage, etc. via subtle structural modifications is an exciting prospect.[1] In general, sterics and/or electronic effects transmitted via mesomeric effects contribute to dramatic variations in the properties. Chromenes, i.e., 2,2-diarylbenzopyrans, are photochromic colorless compounds[2] that undergo photoinduced ring-opening to colored *o*-quinonoid intermediates, which revert slowly in dark to the precursor colorless forms; the colored *o*-quinonoid intermediates may, in principle, exist in four isomeric forms.[3−5] Incidentally, the photogenerated *o*-quinonoid intermediates derived from parent chromene revert rapidly at room temperature to preclude their identification.[3] Benzoannulation has been demonstrated in the literature to render significant stability as well as absorption properties that enable ready recognition of the colored quinonoid forms.[6] There is a significant interest in modulating the spectrokinetic properties of the colored intermediates derived from diarylpyrans from the point of view of application in ophthalmic lenses.[6a] We recently showed that simple arylation may bring about considerable differences in the spectrokinetic properties of the colored reactive *o*-quinonoid intermediates that derive from photoinduced C−O heterolysis.[5b−d] We also demonstrated that the spectrokinetic behavior of the quinonoid intermediates is dramatically influenced when chromenes are constrained to be part of helical scaffolds.[5a]

In continuation of these studies, our attention was drawn to the hexaphenylbenzene scaffold, which has been explored as a structurally rigid core for a variety of phenomena.[7,8] Due to near-orthogonal orientations of the aryl rings, strong electronic interaction between $C_{ipso}-\pi$ orbitals has been shown to manifest in toroidal delocalization of charge in radical cations, cf. Chart 1;[9,10] $C_{ipso}-\pi$ orbital interaction comes into the picture when the ipso carbons attached to the central ring are in a close proximity and are properly oriented to allow partial overlap of the p-orbitals. In hexaarylbenzenes, such an interaction between consecutive ipso carbons attached to the central benzene core may manifest in circular delocalization.[9−11] Similarly, rotatory diffusion of excited states has been exemplified in analogous hexaarylbenzenes.[10a] In addition to their application in deep-blue fluorescent organic light-emitting diodes,[12] the hexaarylbenzene core has been exploited for the synthesis of shape-persistent disk-shaped rigid molecules that measure seven nanometers in diameter,[13] and to organize chromophores to develop triode signal transducers.[14] In light of these investigations, we deemed it quite instructive to examine how the toroidal conjugation via $C_{ipso}-\pi$ orbitals would modify the spectrokinetic properties of photogenerated *reactive* *o*-quinonoid intermediates, when one of the aryl rings in hexaarylbenzene is converted to the latter. Thus, we designed hexarylbenzenes functionalized with a photoreactive 2,2-diarylpyran moiety, i.e., **1**Ch−**3**Ch (Chart 1), which lead to *o*-quinonoid intermediates that are aligned in circular conjugation with the (pentaphenyl)phenyl moiety. The chromenes **1**Ch−**3**Ch differ in terms of the location of the pyran oxygen and afford respective regioisomeric *o*-quinonoid intermediates. Herein, we report the

Received: June 3, 2011
Published: August 03, 2011

Chart 1



synthesis and kinetic behavior of photogenerated colored *o*-quinonoid intermediates of **1**Ch−**3**Ch together with the synthesis and photochemistry of analogous pentamethyl-substituted chromenes **4**Ch−**6**Ch in which the $C_{ipso}-\pi$ orbital conjugation is absent. It is shown that the pentamethylphenyl scaffold in **4**Ch−**5**Ch exerts an effect intriguingly similar to that of the (pentaphenyl)phenyl moiety in **1**Ch−**2**Ch, although marginal stabilization of the *o*-quinonoid intermediates is observed in the latter due supposedly to toroidal conjugation. The C═O···π repulsive interaction appears to account for invisible coloration due to rapid reversion of the *o*-quinonoid intermediates in the case of **3**Ch and **6**Ch.

RESULTS

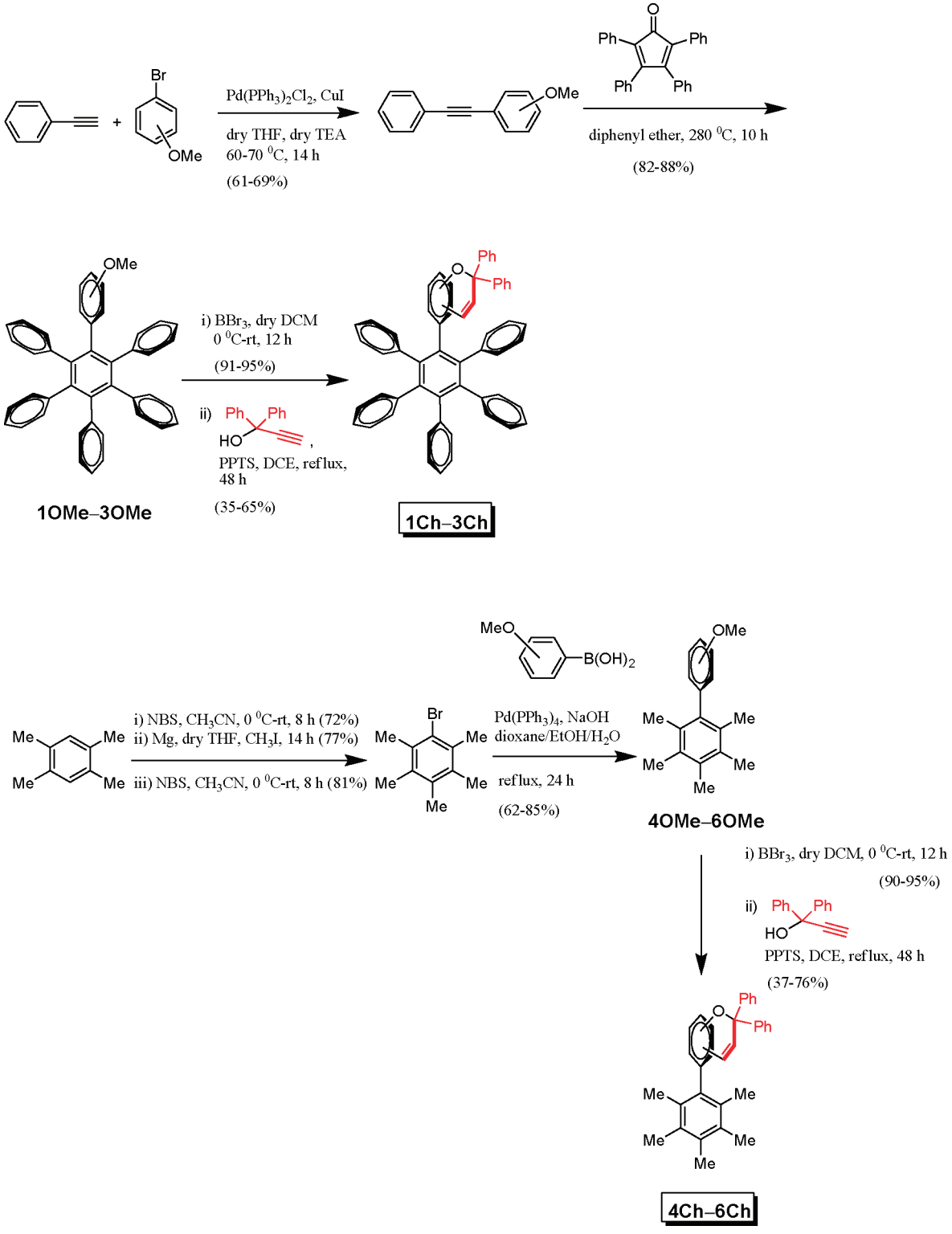
Synthesis of 2,2-Diphenylpyran-Annelated Regioisomeric Photochromic Hexaphenylbenzenes 1Ch−3Ch and Pentamethylphenylchromenes 4Ch−6Ch. The chromenes based on the hexaphenylbenzene scaffold were prepared starting from hydroxy-substituted hexaphenylbenzenes, which were in turn synthesized in a facile manner by Diels−Alder protocol followed by demethylation, cf., Scheme 1.[15] The [4 + 2] cycloaddition between tetraphenylcyclopentadienone and 2-/3-/4-(phenylethynyl)anisole followed by decarbonylation in diphenyl ether led to the corresponding methoxy-substituted hexaphenylbenzenes **1**OMe−**3**OMe. Demethylation using BBr_3/CH_2Cl_2 yielded the corresponding phenols **1**OH−**3**OH, treatment of which with 1,1-diphenylprop-2-yn-1-ol in the presence of a catalyst such as PPTS (pyridinium-*p*-toluenesulfonate) in 1,2-dichloroethane afforded the diphenylpyran-annelated hexaphenylbenzenes **1**Ch−**3**Ch.

The chromenes substituted with a pentamethylphenyl moiety were prepared starting from (pentamethylphenyl)phenols **4**OH−**6**OH, which were in turn synthesized in a facile manner by Suzuki cross-coupling protocol followed by demethylation, cf., Scheme 1. The Suzuki reaction between pentamethylbromobenzene and *o*-/*m*-/*p*-methoxyphenylboronic acid in a 1,4-dioxane/EtOH/H_2O (6:3:1) mixture led to the corresponding methoxy-substituted pentamethylphenylbenzenes **4**OMe−**6**OMe. Demethylation with BBr_3 to the corresponding phenols followed by cyclocondensation with 1,1-diphenylprop-2-yn-1-ol in the presence of PPTS in 1,2-dichloroethane as described above led to pentamethylphenyl-substituted chromenes **4**Ch−**6**Ch. All chromenes **1**Ch−**6**Ch were thoroughly characterized by IR, ^{1}H NMR, ^{13}C NMR, and ESI-MS spectroscopic analyses.

Spectrokinetic Analysis of Photogenerated *o*-Quinonoid Intermediates of Chromenes 1Ch−6Ch. The solutions of arylchromenes **1**Ch−**3**Ch in toluene (10^{-3} M) contained in 3 cm quartz cuvettes equipped with an extended arm were purged thoroughly with nitrogen gas for 30 min and subjected to UV irradiation at $\lambda \simeq 350$ nm at 278 K (for **3**Ch and **6**Ch) and at 293 K (for **1**Ch, **2**Ch, **4**Ch, and **5**Ch) for ca. 1−3 min. The low temperature in the case of **3**Ch and **6**Ch was necessitated by the fact that the colored species underwent rapid reversion at room temperature (298 K) to preclude spectral characterization of the colored forms. Otherwise, the solutions of all chromenes turned orange-red upon UV irradiation. The reversion to colorless forms was found to occur for the intermediates of **1**Ch, **2**Ch, **4**Ch, and **5**Ch within 1−3 min, when stored in the dark at room temperature. The absorption spectra of chromenes **1**Ch−**6**Ch before and after irradiation are shown in Figure 1, which reveals that the irradiation of all chromenes leads to absorption in the visible region; the photogenerated intermediates exhibit a two-band feature, with a rather sharp band toward the shorter wavelength region exhibiting some fine structure and a broad one in the longer wavelength region. A careful inspection shows that the pentamethylphenyl analogs **4**Ch−**6**Ch also exhibit similar spectral features, but that the λ_{max} in the case of **5**Ch and **6**Ch is not well defined. A noteworthy observation is that for chromenes **1**Ch and **4**Ch, the broad visible band is slightly red-shifted relative to those of the remaining chromenes, cf., Table 1.

dx.doi.org/10.1021/jo201144t |*J. Org. Chem.* 2011, 76, 7406–7414

Scheme 1



Thermal Decay Kinetics of *o*-Quinonoid Intermediates. For kinetic analysis of the reactive intermediates, solutions of arylchromenes **1**Ch−**6**Ch (10^{-3} M) in toluene were irradiated for ca. 2−4 min at their absorption maxima with a monochromatic radiation (350 nm from 200-W high-pressure mercury lamp), and the decays of the resultant colored species were monitored at 278 K for **3**Ch and **6**Ch and at 293 K for **1**Ch, **2**Ch, **4**Ch, and **5**Ch by following change in absorbance at the λ_{max} of the colored species with time (in seconds); the coloration plots were developed to ascertain typical irradiation durations required to attain maximum colorability, cf., Supporting Information. As mentioned previously, the intermediates of chromenes **3**Ch and **6**Ch were too labile to

dx.doi.org/10.1021/jo201144t |*J. Org. Chem.* 2011, 76, 7406–7414

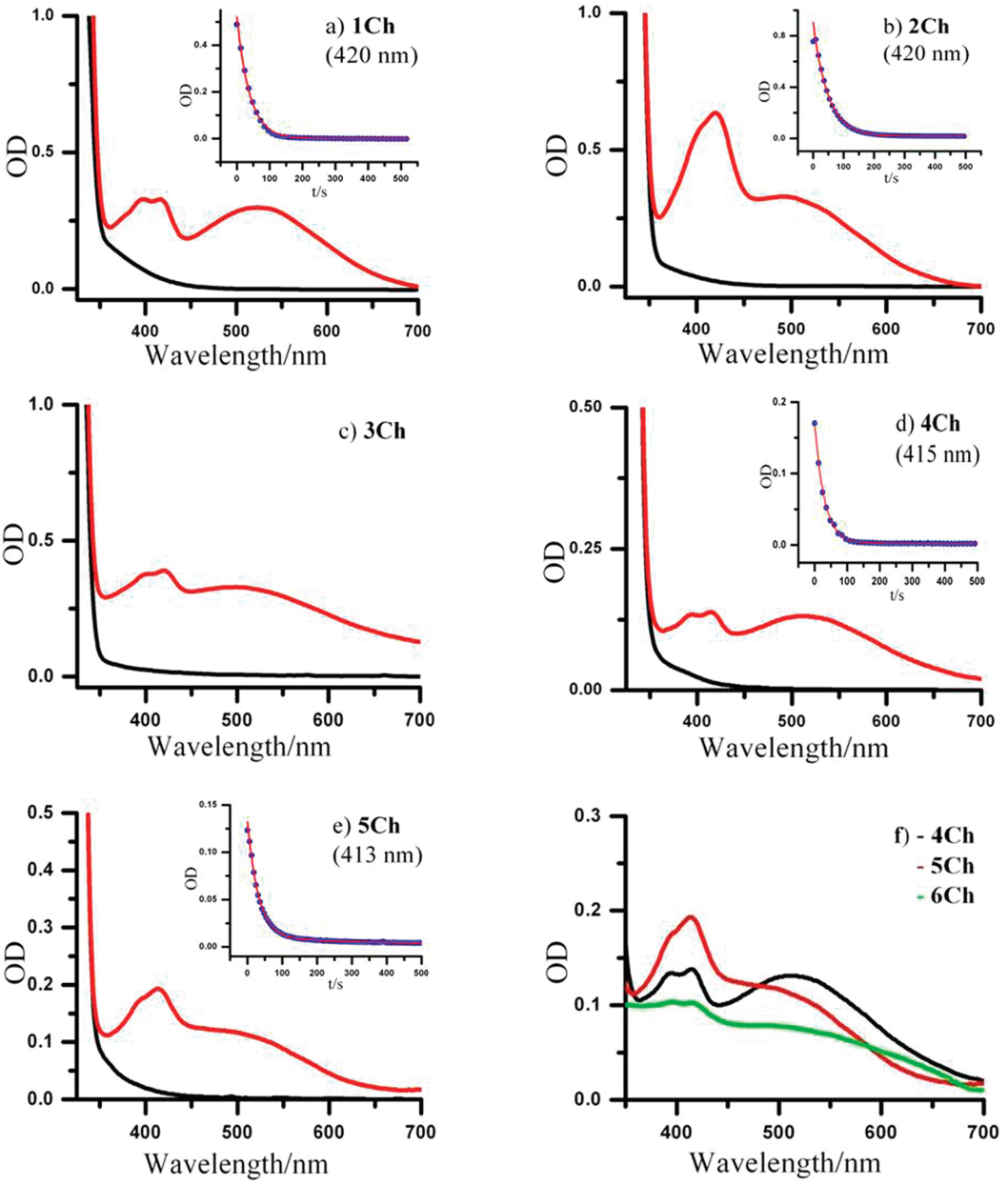


Figure 1. The absorption spectra of chromenes **1**Ch−**5**Ch (black) and their respective photogenerated *o*-quinonoid intermediates (red) (a−e). Also shown in the insets are decay profiles for **1**Ch, **2**Ch, **4**Ch, and **5**Ch, when the absorptions were followed at their longer wavelength absorption maxima given in parentheses, cf., text and Table 1. Overlay of the absorption spectra of the transients of **4**Ch−**6**Ch is shown in panel f.

follow the kinetics at room temperature. The decays of the intermediates of **1**Ch and **2**Ch were fitted to monoexponential function, while those of the intermediates of **4**Ch and **5**Ch could only be fitted to a biexponential function using Levenberg−Marquardt equation. The lifetimes of short-lived as well as the long-lived colored *o*-quinonoid species thus extracted are given in Table 1.

X-ray Crystal Structure Determination of Chromene 5Ch. To assess the extent to which the (pentaphenyl)phenyl/pentamethylphenyl ring is orthogonal to the chromene moiety, attempts were made to crystallize all chromenes and analyze their structures in the solid state. In our efforts, only the crystals of chromene **5**Ch could be readily grown from chloroform−hexane. The X-ray crystal structure determination revealed that the crystals correspond to triclinic crystal system. The perspective drawings of the molecular structure in Figure 2 show that the pentamethylphenyl ring is almost orthogonal to the chromene moiety. The calculated angle between the mean planes of pentamethylphenyl ring and the chromene ring is 76.6°.

DISCUSSION

The *o*-quinonoid intermediates belong to one category of reactive intermediates, and their structurally shorter versions, i.e., *o*-quinone methides,[16] constitute invaluable intermediates in organic synthesis. Given their labile nature, modulation of spectrokinetic properties of reactive intermediates through variation of structural attributes is relevant fundamentally. In particular, the behavior of colored *o*-quinonoid intermediates,

derived from precursor diarylpyrans, is of significant relevance from the point of view of application of the precursor pyrans in ophthalmic lenses as mentioned previously.

It has been shown from several flash photolysis investigations in the pico-[3,4,17] and nanosecond[3,4,17] domains that the diarylpyrans undergo C−O heterolysis in the singlet-excited state[3,4,17] to afford colored species, which are attributed to the so-called *o*-quinonoind intermediates.[3,4] Thus, the species responsible for the color observed upon photolysis of chromenes **1**Ch−**6**Ch are assigned to *o*-quinonoid intermediates. The latter may, in principle, exist in four isomeric conformations as shown in Scheme 2.

The essence of flash photolysis,[17,18] theoretical[19] and ^{19}FNMR spectroscopic investigations[20] on a variety of diarylpyrans is the following: the C−O bond heterolysis occurs in the singlet excited state to generate nonplanar cis−cis (CC) isomer,[17] which evolves from an initially formed charge transfer species. This isomer may collapse back to the closed form or undergo rotation about the C−C single bond to lead to the open transoid form, i.e., trans−cis (TC) isomer; depending upon the nature of the pyran, the bond rotation occurs within 10 ps. In other words, the CC isomer is less likely to persist beyond 10 ps. Thus, it is the TC isomer that is accessible in nanosecond to second time scale. A two-photon absorption brings about geometrical isomerism to the most stable trans−trans (TT) isomer,[17−19] which may further isomerize to the cis−trans (CT) isomer. In general, formation of the TT isomer is minimum in flash photolysis, while it accumulates to a large degree in the steady-state photolysis when irradiated for long time.[5d,18b] It is believed that the CT is unlikely to be populated because of steric interactions that increase the energy.[4,5d] Indeed, the CC and CT isomers are discarded as being unimportant when analyzing the transients in nanosecond to second time scale. In light of the established kinetic behavior of *o*-quinonoid intermediates, we believe that only TC and TT isomers should be relevant in the analysis of the transients of pentamethyl/pentaphenyl-functionalized chromenes **1**Ch−**6**Ch, when the latter are subjected to irradiation. In particular, it is the TC isomer that should be predominantly formed when the photolysis is carried out for a shorter duration as in the present investigation, which limits the build-up of TT isomer. Thus, only TC should be considered as being relevant uniformly for all the chromenes **1**Ch−**6**Ch and their kinetics.

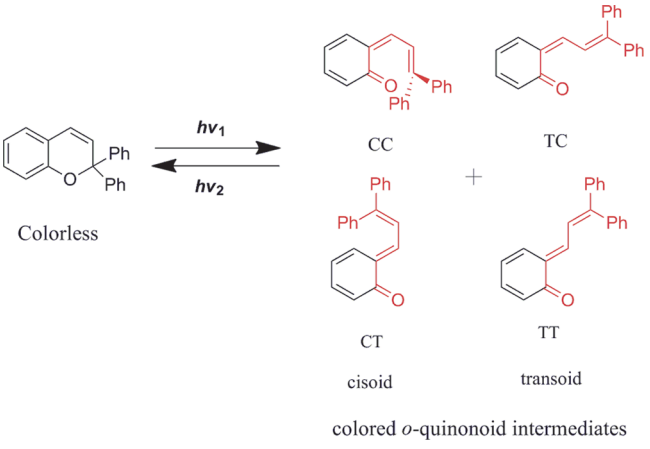
The absorption spectra of all the *o*-quinonoid intermediates of **1**Ch−**6**Ch show that the differences in the absorptions are very unremarkable. In the case of the intermediates of **1**Ch and **2**Ch, one observes a marginal red-shift by 3−12 nm for both ca. 410- and 500-nm bands, when compared with those of the analogous intermediates of **4**Ch and **5**Ch, cf. Table 1. The X-ray crystal structure analysis of one of the compounds, i.e., **5**Ch, shows that the pentamethylphenyl ring is almost orthogonal to the chromene moiety. In a similar manner, the (pentaphenyl)phenyl ring in **1**Ch−**3**Ch should also be expected to be orthogonal to the chromene moiety. Indeed, we have analyzed the structures of hexaarylbenzene derivatives reported in the Cambridge Structural Database (CSD)[21] and found that the (pentaphenyl)phenyl ring orients with respect to the core aryl moiety at an angle that varies between 60° and 90°. Thus, the pentamethylphenyl as well as (pentaphenyl)phenyl substituents of chromenes cannot be expected to be significantly involved in the mesomeric effect. How then does the pentamethylphenyl substitutent that orients almost orthogonally to the *o*-quinonid intermediates of **4**Ch and **5**Ch stabilize the latter? It should be emphasized that the intermediate in the case of the parent chromene that is

Table 1. Spectrokinetic Properties of the Chromenes 1Ch−6Ch and Their Photogenerated Colored Intermediates

compound	before *hν* (nm) (*ε*)	after *hν* λ_{max} (nm)[a]	rate constants k_1 and k_2 (s^{-1})
1Ch	316 (sh, 1740)[b]	417, 524	0.026[c]
2Ch	319 (16500)	420, 494	0.019[c]
3Ch	318 (4820)	420, 498	*d*
4Ch	318 (4640)	415, 512	0.033, 0.0008
5Ch	321 (13440)	413[e]	0.032, 0.0018
6Ch	313 (6380)	414[e]	*d*

[a] The long wavelength absorption maximum corresponds to the broad band. [b] sh = shoulder. [c] Fitted to single exponential function. [d] The rapid reversion precluded kinetic monitoring, see text. [e] The longer wavelength band is ill defined.

Scheme 2



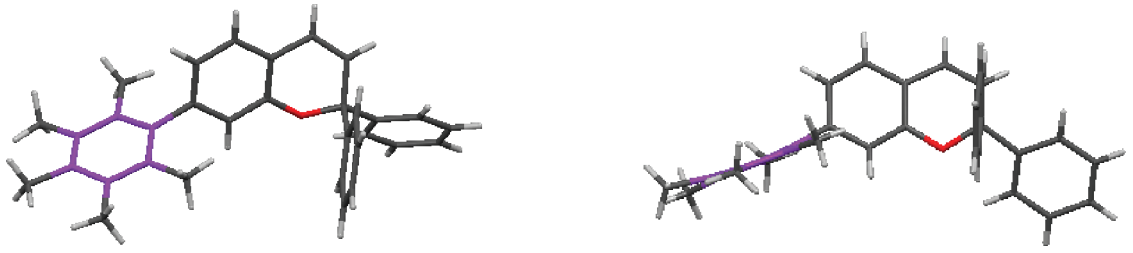


Figure 2. The X-ray determined molecular structures of chromene **5**Ch. Notice that the pentamethylphenyl ring is almost orthogonal to the chromene moiety.

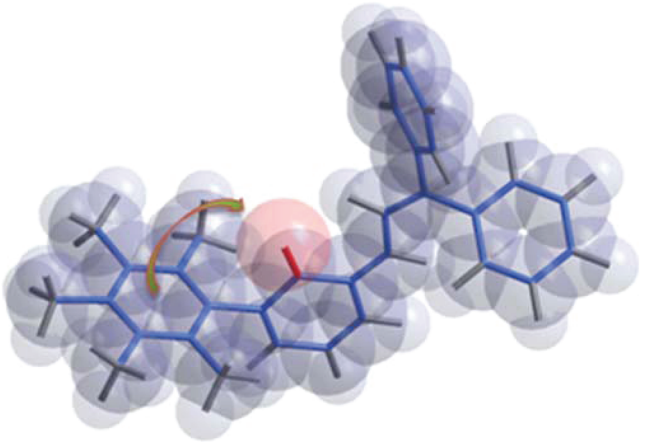


Figure 3. The AM1-minimized structure of the TC isomer of **6**Ch to exemplify the repulsive interaction between quinonoid oxygen and p-orbitals of the pentamethylphenyl core.

devoid of any substituents is very short-lived, as in the case of **3**Ch and **6**Ch, and precludes detection at room temperature. The kinetic behavior of the intermediates of **3**Ch and **6**Ch is most compelling; the visible coloration that is observed during the photolysis of the solutions of these chromenes vanishes as soon as the radiation is turned off. The intermediates revert too rapidly at room temperature (298 K) to preclude kinetic follow-up. What is it that causes the intermediates of **3**Ch and **6**Ch to be so short-lived in light of the fact that the pentamethylphenyl/(pentaphenyl)phenyl rings in these cases also are expected a priori to be orthogonal?

As mentioned previously, the *o*-quinonoid intermediate of the parent chromene is very short-lived at room temperature.[3] The strategies to render the *o*-quinonoid intermediates as rather longer-lived include benzoannulation, fluorene-annulation, arylation at 6- and 7-positions, etc.[5,6,22] It is indeed intriguing that the intermediates of **1**Ch, **2**Ch, **4**Ch, and **5**Ch exhibit considerably enhanced persistence given that the (pentaphenyl)phenyl/pentamethylpheny moieties are orthogonal to the chromene. In view of fast decay of the CC isomer and inaccessibility of the CT isomer (Scheme 2) as mentioned previously, the rate constants k_1 and k_2 extracted from kinetic monitoring may be assigned to TC and TT, respectively. As the TT isomer is populated only to a negligible/minor degree by a two-photon process, it may be considered as insignificant. Thus, the kinetic data in Table 1 show that the values of rate constant k_1, attributed to TC isomer, for all cases are significantly longer and compare well with those reported for the TC isomers derived from aryl-substituted chromenes or naphthopyrans in which the mesomeric effects decisively stabilize the *o*-quinonoid intermediates.[4,5a−c,22] Given that the mesomeric effects are not possible in all the intermediates of chromenes **1**Ch, **2**Ch, **4**Ch, and **5**Ch, we believe that intramolecular charge-transfer is likely to be the origin of the observed stabilization of the photogenerated *o*-quinonoid intermediates. Inspection of the absorption data and the decay rate constants (k_1) in Table 1 for the intermediates of **1**Ch, **2**Ch, **4**Ch, and **5**Ch reveals that the intermediates of **1**Ch and **2**Ch are slightly red-shifted and decay rather slowly relative to those of **4**Ch and **5**Ch. This marginal, yet meaningful stabilization of the intermediates of **1**Ch and **2**Ch, we believe, arises from $C_{ipso}-\pi$ stabilization.

The reason for rapid reversion of the intermediates of **3**Ch and **6**Ch at room temperature becomes evident from a closer inspection of the structures of their TC isomers of their *o*-quinonoid intermediates. The AM1-minimized structure of the *o*-quinonoid intermediate of **6**Ch is shown in Figure 3, which reveals that the quinonoid oxygen in these cases is restrained to lie over the pentamethylphenyl or (pentaphenyl)phenyl ring. Thus, there should be considerable unfavorable electronic repulsion between the oxygen lone-pair and the benzene p-orbitals. This is likely to be the source of rapid reversion of the *o*-quinonoid intermediate to the colorless closed form, such that the molecules relieve themselves of high-energy by undergoing fast bond rotations.[23] Clearly, stereoelectronic control of the persistence of reactive intermediates, i.e, *o*-quinonemethide derivatives, is compellingly evident from subtle structural modifications.

CONCLUSIONS

Regioisomeric hexaphenylbenzenes functionalized with 2,2-diphenylpyran **1**Ch−**3**Ch were synthesized and their photochromic behavior investigated to explore the extent to which the possible $C_{ipso}-\pi$ circular conjugation may stabilize the *o*-quinonoid reactive intermediates derived from photoexcitation. Analogous pentamethylphenyl chromenes **4**Ch−**6**Ch were also synthesized and their photobehavior examined. Upon photoirradiation, the solutions of all chromenes **1**Ch−**6**Ch exhibited orange-red color, which is attributed to the formation of *o*-quinonoid intermediates. In the case of chromenes **3**Ch and **6**Ch, reversion of the reactive intermediates was found to occur too rapidly at room temperature to preclude any visible coloration. However, the intermediates of chromenes with (pentaphenyl)phenyl as well as pentamethylphenyl substitution at 6- and 7-positions, i.e., **1**Ch, **2**Ch, **4**Ch, and **5**Ch, were found to exhibit considerable stability; we believe that the latter is due to intramolecular charge transfer from orthogonally oriented pentaphenylphenyl/pentamethylphenyl rings to the quinonoid moiety. Among **1**Ch, **2**Ch, **4**Ch, and **5**Ch, the intermediates of **1**Ch and **2**Ch were found to show comparatively longer persistence and slightly red-shifted absorptions as compared to those of the pentamethylphenyl analogues, i.e., **4**Ch and **5**Ch. The marginal stabilization presumably arises from $C_{ipso}-\pi$ circular conjugation. The reason for rapid reversion of the intermediates of **3**Ch and **6**Ch should be reconciled from electronic repulsion between the lone-pairs of the quionoid oxygen and the p-orbitals of the (pentaphenyl)phenyl/pentamethylphenyl ring. Thus, stereoelectronic control of the persistence of reactive *o*-quinonoid intermediates that are generated photochemically is demonstrated via substitution of chromene with sterically hindered pentaphenylphenyl/pentamethylphenyl scaffolds.

EXPERIMENTAL SECTION

General Aspects. 1,2-Dichloroethane was distilled over calcium hydride under nitrogen prior to use. Anhydrous tetrahydrofuran (THF) and toluene were freshly distilled over sodium prior to use and purged with nitrogen gas. All other solvents were distilled before use. Column chromatography was conducted with 60−120 mesh silica gel.

General Procedure for the Synthesis of 2-/3-/4-Hydroxyhexaphenylbenzenes 1OH−3OH. An oven-dried pressure tube was charged with 3 mL of dry THF, 3 mL of dry triethylamine, 2-/3-/4-bromoanisole (0.50 g, 2.67 mmol), phenylacetylene (0.30 g, 2.94 mmol), $Pd(PPh_3)_2Cl_2$ (0.04 g, 0.05 mmol), and CuI (0.01 g, 0.053

mmol) under nitrogen. The contents were heated at 60−70 °C for 14 h. Subsequently, the tube was cooled and the organic matter was diluted with DCM and washed with 10% HCl. The organic portion was further treated with brine, dried over anhyd Na_2SO_4, filtered, and evaporated to yield the crude product, which was further purified by silica gel column chromatography to obtain pure 2-/3-/4-(phenylethynyl)anisoles. The yields were typically 61−69%.

2-/3-/4-(Phenylethynyl)anisole (0.26 g, 1.25 mmol) obtained above was taken in diphenyl ether along with tetraphenylcyclopentadienone (0.48 g, 1.25 mmol) and heated under N_2 for 10 h. The contents were diluted with petroleum ether, and the product was obtained by filtration and subsequent washing. The crude product was further purified by silica-gel column chromatography to furnish 2-/3-/4-methoxyhexaphenylbenzene (**1**OMe/**2**OMe/**3**OMe) as a colorless solid in ca. 80−85% isolated yield.

2-/3-/4-Methoxyhexaphenylbenzene (0.27 g, 0.48 mmol) thus obtained above was treated with BBr_3 (0.15 mL, 1.60 mmol) in dry DCM (10 mL) at 0 °C. The reaction was slowly allowed to attain room temperature over a period of 12 h. Subsequently, the reaction mixture was poured into crushed ice, and the organic matter was extracted with DCM. The combined extract was washed thoroughly with brine, dried over anhyd Na_2SO_4, and filtered, and solvent was removed in vacuo to afford the crude product. Further purification with silica-gel column chromatography yielded pure 2-/3-/4-hydroxyhexaphenylbenzene ((**1**OH/**2**OH/**3**OH) in 90−95% yield.

General Procedure for the Synthesis of 2,2-Diphenylpyran-Annelated Regioisomeric Photochromic Hexaphenylbenzenes 1Ch−3Ch. All the photochromic diphenylpyrans based on hexaphenylbenzene scaffold **1**Ch−**3**Ch were prepared by following the literature-reported procedure.[24] A representative procedure for the synthesis of chromene **2**Ch is described below.

A mixture of 3-hydroxyhexaphenylbenzene **2**OH (0.17 mmol), 1,1-diphenylprop-2-yn-1-ol (0.34 mmol) and a catalytic amount of pyridinium-*p*-toluene sulfonate (PPTS, 5 mol %) was added to dry 1,2-dichloroethane (6 mL). The reaction mixture was heated at reflux under nitrogen gas atmosphere for 48 h. After this period, the contents were cooled, washed with saturated Na_2CO_3 solution, and the organic matter was extracted with chloroform (20 mL × 3). The combined extract was dried over anhyd Na_2SO_4, filtered and evaporated to yield the crude compound, which was further purified by silica-gel column chromatography, yield 40%.

4-(Phenylethynyl)anisole:[25] Pale yellow solid, yield 65%; mp 54−56 °C (lit. mp 56−58 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.89 (d, J = 8.8 Hz, 2H), 7.30−7.37 (m, 3H), 7.47−7.54 (m, 4H).

4-Methoxyhexaphenylbenzene,[15] ***1**OMe*. Colorless solid, yield 88%; mp >300 °C; IR (KBr) cm^{-1} 3031, 1607, 1510, 1441, 1402, 1246; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.6 (s, 3H), 6.40 (d, J = 7.3 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 6.82- 6.89 (m, 25H).

4-Hydroxyhexaphenylbenzene,[15] ***1**OH*. Colorless solid, yield 95%; mp >300 °C; IR (KBr) cm^{-1} 3520, 3057, 1603, 1512, 1403; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 6.83−6.86 (m, 25H).

2,2-Diphenylpyran-Annelated Hexaphenylbenzene, ***1**Ch*. Pale yellow solid, yield 65%; mp >300 °C; IR (KBr) cm^{-1} 3027, 1949, 1606, 1495, 1408, 1240; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (d, J = 9.8 Hz, 1H), 6.24 (d, J = 9.8 Hz, 1H), 6.38−6.40 (m, 2H), 6.50 (dd, J_1 = 8.2 Hz, J_2 = 2.1 Hz, 1H), 6.74−6.84 (m, 25 H), 7.23−7.29 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.3, 114.9, 119.8, 123.8, 125.0, 125.1, 126.5, 126.6, 126.9, 127.2, 127.9, 128.5, 129.5, 131.28, 131.32, 131.38, 131.4, 132.4, 133.6, 139.8, 140.1, 140.39, 140.4, 140.58, 140.6, 144.5, 150.0; ESI-MS$^+$ m/z Calcd for $C_{57}H_{40}O$ 758.3425 [M + NH_4^+], found 758.3425.

3-(Phenylethynyl)anisole:[26] Yellow solid, yield 69%; mp 74−75 °C (lit. mp 77−78 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.9 (dd, J_1 = 8.3 Hz, J_2 = 2.7 Hz, 1H), 7.06−7.07 (m, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.24−7.28 (m, 1H), 7.34−7.38 (m, 3H), 7.52−7.55 (m, 2H).

3-Methoxyhexaphenylbenzene, ***2**OMe*. Colorless solid, yield 82%; mp >300 °C; IR (KBr) cm^{-1} 3026, 1599, 1436, 1245; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 (s, 3H), 6.39−6.43 (m, 3H), 6.74−6.77 (m, 1H), 6.83−6.87 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.0, 111.9, 116.6, 124.3, 125.1, 125.2, 126.5, 126.6, 127.4, 131.2, 131.3, 131.4, 140.0, 140.2, 140.3, 140.5, 140.6, 141.7, 158.1; ESI-MS$^+$ m/z Calcd for $C_{43}H_{32}O$ 565.2531 [M + H], found 565.2537.

3-Hydroxyhexaphenylbenzene, ***2**OH*. Colorless solid, yield 93%; mp >300 °C; IR (KBr) cm^{-1} 3530, 3032, 1584, 1401, 1260; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.31−6.32 (m, 2H), 6.43 (d, J = 7.4 Hz, 1H), 6.71−6.74 (m, 1H), 6.83−6.86 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 112.2, 118.5, 124.4, 125.2, 125.3, 126.6, 127.7, 131.2, 131.27, 131.3, 131.4, 140.1, 140.23, 140.29, 140.37, 140.39, 140.48, 140.52, 140.7; ESI-MS$^+$ m/z Calcd for $C_{42}H_{30}O$ 551.2375 [M + H], found 551.2372.

2,2-Diphenylpyran-Annelated Hexaphenylbenzene, ***2**Ch*. Colorless solid, yield 40%; mp >300 °C; IR (KBr) cm^{-1} 3027, 1949, 1606, 1495, 1408, 1240; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 (d, J = 9.7 Hz, 1H), 6.31 (dd, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1H), 6.36 (d, J = 9.7 Hz, 1H), 6.47 (d, J = 7.6 Hz, 2H), 6.77−6.85 (m, 25H), 7.22−7.30 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.2, 118.1, 119.7, 123.4, 124.6, 124.7, 125.1, 125.2, 126.4, 126.5, 126.6, 126.8, 127.2, 127.8, 127.9, 131.2, 131.3, 131.37, 131.4, 139.7, 140.1, 140.2, 140.3, 140.6, 142.2, 144.9, 151.3; ESI-MS$^+$ m/z Calcd for $C_{57}H_{40}O$ 741.3157 [M + H], found 741.3157.

2-(Phenylethynyl)anisole.[27] Yellow oil, yield 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 6.89−6.96 (m, 2H), 7.29−7.36 (m, 4H), 7.50 (d, J = 7.6 Hz, 1H), 7.55−7.57 (m, 2H).

2-Methoxyhexaphenylbenzene, ***3**OMe*. Colorless solid, yield 83%; mp >300 °C; IR (KBr) cm^{-1} 3027, 2931, 1597, 1496, 1438, 1246; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.41 (s, 3H), 6.37 (d, J = 8.2 Hz, 1H), 6.52 (t, J = 7.6 Hz, 1H), 6.81−6.90 (m, 27H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 54.7, 109.5, 119.1, 125.0, 125.1, 126.0, 126.3, 126.4, 126.5, 127.5, 129.9, 130.8, 130.9, 131.4, 131.5, 131.6, 132.6, 137.1, 139.9, 140.0, 140.7, 140.8, 156.4; ESI-MS$^+$ m/z Calcd for $C_{43}H_{32}O$ 565.2531 [M + H], found 565.2534.

2-Hydroxyhexaphenylbenzene, ***3**OH*. Colorless solid, yield 91%; mp >300 °C; IR (KBr) cm^{-1} 3427, 3026, 1598, 1496, 1443, 1400, 1173; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.45−6.47 (m, 1H), 6.49−6.52 (m, 1H), 6.80−6.90 (m, 27H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 114.5, 119.4, 125.3, 125.7, 126.5, 126.6, 126.9, 127.4, 128.2, 129.9, 131.1, 131.2, 131.3, 132.1, 134.6, 139.7, 140.1, 140.2, 140.9, 141.4, 141.6, 152.1; ESI-MS$^+$ m/z Calcd for $C_{42}H_{30}O$ 551.2375 [M + H], found 551.2372.

2,2-Diphenylpyran-Annelated Hexaphenylbenzene, ***3**Ch*. Pale yellow solid, yield 35%; mp >300 °C; IR (KBr) cm^{-1} 3030, 1594, 1493, 1439, 1226; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (d, J = 9.8 Hz, 1H), 6.15 (d, J = 6.7 Hz, 2H), 6.37−6.41 (m, 2H), 6.55 (t, J = 6.6 Hz, 2H), 6.62 (dd, J_1 = 7.3 Hz, J_2 = 1.5 Hz, 1H), 6.67 (dd, J_1 = 7.6 Hz, J_2 = 1.8 Hz, 1H), 6.73−6.86 (m, 21H), 7.29−7.39 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.4, 118.9, 119.3, 123.1, 124.9, 125.0, 125.9, 126.2, 126.41, 126.44, 126.47, 126.5, 127.6, 127.9, 128.0, 128.2, 131.3, 131.4, 131.5, 131.7, 133.6, 135.9, 139.8, 140.1, 140.2, 140.7, 140.8, 145.5, 149.6; ESI-MS$^+$ m/z Calcd for $C_{57}H_{40}O$ 741.3157 [M + H], found 741.3150.

General Procedure for the Synthesis of (Pentamethylphenyl)phenols 4OH-6OH by Suzuki Coupling. A representative procedure for the preparation of 2-(pentamethylphenyl)phenol **6**OH is described below.

In an oven-dried two-necked round-bottomed flask were placed 12 mL of distilled 1,4-dioxane, 6 mL of ethanol, and 2 mL of water, which was then purged thoroughly with N_2 gas for 30 min. Pentamethylbromobenzene (0.50 g, 2.2 mmol), 2-methoxyphenylboronic acid (0.50 g, 3.3 mmol), $Pd(PPh_3)_4$ (0.25 g, 0.22 mmol), and NaOH (0.35 g, 0.8.8 mmol) were introduced into the round-bottomed flask under nitrogen. The contents were heated at 100−110 °C for 24 h. Subsequently, the reaction

mixture was cooled, 1,4-dioxane and ethanol were removed in vacuo, and the mixture was extracted with $CHCl_3$. The organic portion was further treated with brine, dried over anhyd Na_2SO_4, and filtered and the solvent removed to yield the crude product, which was purified by silica gel column chromatography to obtain pure 2-(pentamethylphenyl)anisole **6**OMe as a colorless solid (0.35 g, 62%). The demethylation as described above led to the corresponding phenol in >90% isolated yield.

4-(Pentamethylphenyl)anisole, ***4****OMe.* Colorless solid, yield 85%; mp 110−113 °C; IR (KBr) cm^{-1} 2923, 2852, 1608, 1512, 1455, 1284, 1245; ^1H NMR (500 MHz, $CDCl_3$) δ 1.96 (s, 6H), 2.26 (s, 6H), 2.30 (s, 3H), 3.86 (s, 3H), 6.95 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 16.8, 18.4, 55.2, 113.6, 130.5, 132.1, 132.3, 133.9, 135.3, 139.4, 157.9; ESI-MS$^+$ m/z Calcd for $C_{18}H_{22}O$ 255.1749 [M + H], found 255.1743.

4-(Pentamethylphenyl)phenol, ***4****OH.* Colorless solid, yield 95%; mp 127−129 °C; IR (KBr) cm^{-1} 3323, 2920, 2852, 1597, 1512, 1442, 1233; ^1H NMR (500 MHz, $CDCl_3$) δ 1.96 (s, 6H), 2.26 (s, 6H), 2.31 (s, 3H), 6.87−6.89 (m, 2H), 6.97−6.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 16.8, 18.3, 115.1, 130.7, 132.1, 132.3, 133.9, 135.5, 139.3, 153.8; ESI-MS$^+$ m/z Calcd for $C_{17}H_{20}O$ 241.1592 [M + H], found 241.1591.

Pentamethylphenylchromene, ***4****Ch.* Colorless solid, yield 76%; mp 160−163 °C; IR (KBr) cm^{-1} 3054, 3025, 2920, 1486, 1446, 1236, 1213; ^1H NMR (500 MHz, $CDCl_3$) δ 1.94 (s, 6H), 2.24 (s, 6H), 2.29 (s, 3H), 6.19 (d, J = 9.7 Hz, 1H), 6.59 (d, J = 9.7 Hz, 1H), 6.74 (d, J = 1.7 Hz, 1H), 6.86 (dd, J_1 = 8.3 Hz, J_2 = 2.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 7.27−7.30 (m, 2H), 7.33−7.37 (m, 4H), 7.47−7.49 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 16.8, 18.5, 82.7, 116.1, 120.5, 123.4, 127.0, 127.4, 127.6, 128.1, 128.5, 130.7, 132.1, 132.3, 133.9, 135.8, 139.2, 145.1, 150.9; ESI-MS$^+$ m/z Calcd for $C_{32}H_{30}O$ 431.2375 [M + H], found 431.2377.

3-(Pentamethylphenyl)anisole, ***5****OMe.* Colorless solid, yield 70%; mp 69−70 °C; IR (KBr) cm^{-1} 2924, 1586, 1486, 1462, 1418, 1233; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 6H), 2.26 (s, 6H), 2.31 (s, 3H), 3.81 (s, 3H), 6.68−6.73 (m, 2H), 6.86−6.89 (m, 1H), 7.30−7.34 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 16.8, 18.3, 55.1, 111.8, 114.9, 121.9, 129.2, 131.5, 132.3, 134.0, 139.7, 144.4, 159.5; ESI-MS$^+$ m/z Calcd for $C_{18}H_{22}O$ 255.1749 [M + H], found 255.1748.

3-(Pentamethylphenyl)phenol, ***5****OH.* Colorless solid, yield 92%; mp 109−111 °C; IR (KBr) cm^{-1} 3464, 2991, 2921, 1594, 1443, 1238, 1195; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 6H), 2.27 (s, 6H), 2.32 (s, 3H), 4.79 (s, 1H), 6.60−6.61 (m, 1H), 6.71 (d, J = 7.6 Hz, 1H) 6.80−6.83 (m, 1H), 7.29 (t, J = 8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 16.8, 18.3, 113.2, 116.4, 122.2, 129.5, 131.5, 132.3, 134.0, 139.3, 144.8, 155.3; ESI-MS$^+$ m/z Calcd for $C_{17}H_{20}O$ 241.1592 [M + H], found 241.1591.

Pentamethylphenylchromene, ***5****Ch.* Colorless solid, yield 73%; mp 150−152 °C; IR (KBr) cm^{-1} 3026, 2919, 1486, 1446, 1235, 1213; ^1H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 6H), 2.25 (s, 6H), 2.29 (s, 3H), 6.27 (d, J = 9.8 Hz, 1H), 6.60 (dd, J_1 = 7.4 Hz, J_2 = 1.5 Hz, 1H), 6.67 (d, J = 9.6 Hz, 1H), 6.73 (s, 1H), 7.03 (d, J = 7.5 Hz, 1H), 7.25−7.28 (m, 2H), 7.31−7.34 (m, 4H), 7.44−7.48 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 16.8, 18.2, 82.2, 117.9, 119.4, 122.6, 123.4, 126.3, 127.0, 127.4, 128.0, 128.7, 131.4, 132.3, 133.9, 139.4, 144.7, 144.9, 152.5; ESI-MS$^+$ m/z Calcd for $C_{32}H_{30}O$ 431.2375 [M + H], found 431.2376.

2-(Pentamethylphenyl)anisole, ***6****OMe.* Colorless solid, yield 62%; mp 65−66 °C; IR (KBr) cm^{-1} 3004, 2924, 2831, 1596, 1578, 1491, 1459, 1431, 1231; ^1H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 6H), 2.27 (s, 6H), 2.31 (s, 3H), 3.76 (s, 3H), 6.99−7.02 (m, 3H), 7.33−7.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 16.9, 17.9, 55.4, 110.6, 120.5, 127.9, 131.2, 131.4, 131.9, 132.1, 133.9, 135.8, 156.8; ESI-MS$^+$ m/z Calcd for $C_{18}H_{22}O$ 255.1749 [M + H], found 255.1743.

2-(Pentamethylphenyl)phenol, ***6****OH.* Colorless solid, yield 90%; mp 108−110 °C; IR (KBr) cm^{-1} 3520, 2924, 1579, 1485, 1456, 1197, 1170; ^1H NMR (400 MHz, $CDCl_3$) δ 1.96 (s, 6H), 2.26 (s, 6H), 2.31 (s, 3H), 6.97−7.00 (m, 3H), 7.25−7.29 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 16.8, 17.8, 114.8, 120.5, 128.4, 128.6, 130.3, 132.0, 133.18, 133.19, 135.4, 152.6; ESI-MS$^+$ m/z Calcd for $C_{17}H_{20}O$ 241.1592 [M + H], found 241.1593.

Pentamethylphenylchromene, ***6****Ch.* Colorless solid, yield 37%; mp 69−70 °C; IR (KBr) cm^{-1} 3026, 2919, 1486, 1446, 1235, 1213; ^1H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 6H), 2.24 (s, 6H), 2.29 (s, 3H), 6.09 (d, J = 9.7 Hz, 1H), 6.67 (d, J = 10.0 Hz, 1H), 6.86−6.89 (m, 2H), 7.00−7.02 (m, 1H), 7.16−7.21 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 16.8, 18.2, 82.1, 120.9, 121.3, 123.8, 125.2, 126.7, 127.1, 127.9, 128.8, 130.9, 131.3, 131.8, 132.1, 133.6, 135.2, 145.3, 149.3; ESI-MS$^+$ m/z Calcd for $C_{32}H_{30}O$ 431.2375 [M + H], found 431.2376.

■ ASSOCIATED CONTENT

Supporting Information. Coloration plots, and ^1H and ^{13}C NMR spectral reproductions for all the important intermediates and final compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: moorthy@iitk.ac.in.

■ ACKNOWLEDGMENT

J.N.M. is thankful to CSIR (Council of Scientific and Industrial Research), India, for funding. S.M. and K.N.P. are grateful to CSIR for senior and junior research fellowships, respectively. We thank Mr. Ankur Roy and Mr. Rajeev Kumar for initial experiments.

DEDICATION

†This paper is dedicated to Prof. N. Sathyamurthy on the occasion of his 60th birth day.

■ REFERENCES

(1) (a) Bertelson, R. C. In *Photochromism*; Brown, G. H., Ed.; Wiley: New York, 1971; Chapter 10 and references therein. (b) Kawauchi, S.; Yoshida, H.; Yamashina, N.; Ohira, M.; Saeda, S.; Irie, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 267. (c) Takeshita, M.; Kato, N.; Kawauchi, S.; Imase, T.; Watanabe, J.; Irie, M. *J. Org. Chem.* **1998**, *63*, 9306. (d) Irie, M., Ed. Special Issue: Photochromism: Memories and Switches. *Chem. Rev.* **2000**, *100*, 1683. (e) Taneda, M.; Koyama, H.; Kawato, T. *Chem. Lett.* **2007**, *36*, 354. (f) Kawato, T.; Amimoto, K.; Maeda, H.; Koyama, H.; Kanatomi, H. *Mol. Cryst. Liq. Cryst.* **2000**, *345*, 57. (g) Raymo, F. M.; Giordani, S. *Org. Lett.* **2001**, *3*, 1833. (h) Raymo, F. M.; Giordani, S. *Org. Lett.* **2001**, *3*, 3475. (i) Raymo, F. M.; Tomasulo, M. *Chem.—Eur. J.* **2006**, *12*, 3186. (j) Callan, J. F.; de Silvaa, A. P.; Magria, D. C. *Tetrahedron* **2005**, *61*, 8551. (k) di Nunzio, M. R.; Gentili, P. L.; Romani, A.; Favaro, G. *J. Phys. Chem. C* **2010**, *114*, 6123. (l) di Nunzio, M. R.; Romani, A.; Favaro, G. *J. Phys. Chem. A* **2009**, *113*, 9424. (m) Gentili, P. L.; Ortica, F.; Favaro, G. *J. Phys. Chem. B* **2008**, *112*, 16793. (n) Al-Atar, U.; Fernandes, R.; Johnsen, B.; Baillie, D.; Branda, N. R. *J. Am. Chem. Soc.* **2009**, *131*, 15966. (o) Amimoto, K.; Kawato, T. *J. Photochem. Photobiol. C* **2005**, *6*, 207. (p) Finden, J.; Kunz, T. K.; Branda, N. R.; Wolf, M. O. *Adv. Mater.* **2008**, *20*, 1998. (q) Peters, A.; Vitols, C.; McDonald, R.; Branda, N. R. *Org. Lett.* **2003**, *5*, 1183. (r) Zhao, H.; Al-Atar, U.; Pace, T. C. S.; Bohne, C.; Branda, N. R. *J. Photochem. Photobiol. A* **2008**, *200*, 74. (s) Choi, S. W.; Kawauchi, S.; Ha, N. Y.; Takezoe, H. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3671. (t) Boyer, J. C.; Carling, C. J.; Gates, B. D.; Branda, N. R. *J. Am. Chem. Soc.* **2010**, *132*, 15766.

(2) (a) *Photochromism: Molecules and Systems*; Durr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990. (b) *Organic Photochromic*

and Thermochromic Compounds; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum Press: New York, 1999; Vols. 1 and 2.

(3) Lenoble, C.; Becker, R. S. *J. Photochem.* **1986**, *33*, 187.

(4) (a) Kodama, Y.; Nakabayashi, T.; Segawa, K.; Hattori, E.; Sakuragi, M.; Nishi, N.; Sakuragi, H. *J. Phys. Chem. A* **2000**, *104*, 11478. (b) Hobley, J.; Malatesta, V.; Hatanaka, K.; Kajimoto, S.; Williams, S. L.; Fukumura, H. *Phys. Chem. Chem. Phys.* **2002**, *4*, 180. (c) Gentili, P. L.; Danilov, E.; Ortica, F.; Rodgers, M. A. J.; Favaro, G. *Photochem. Photobiol. Sci.* **2004**, *3*, 886.

(5) (a) Moorthy, J. N.; Venkatakrishnan, P.; Sengupta, S.; Baidya, M. *Org. Lett.* **2006**, *8*, 4891. (b) Moorthy, J. N.; Venkatakrishnan, P.; Samanta, S.; Kumar, D. K. *Org. Lett.* **2007**, *9*, 919. (c) Moorthy, J. N.; Venkatakrishnan, P.; Samanta, S. *Org. Biomol. Chem.* **2007**, *5*, 1354. (d) Moorthy, J. N.; Koner, A. L.; Samanta, S.; Roy, A.; Nau, W. M. *Chem.—Eur. J.* **2009**, *15*, 4289.

(6) (a) Crano, J. C.; Flood, T.; Knowles, D.; Kumar, A.; Gemert, B. V. *Pure Appl. Chem.* **1996**, *68*, 1395. (b) Pozzo, J.-L.; Samat, A.; Guglielmetti, R.; Lokshin, V.; Minkin, V. *Can. J. Chem.* **1996**, *74*, 1649. (c) Pozzo, J.-L.; Lokshin, V.; Samat, A.; Guglielmetti, R.; Dubest, R.; Aubard, J. *J. Photochem. Photobiol. A* **1998**, *114*, 185. (d) Oliveira, M. M.; Carvalho, L. M.; Moustrou, C.; Samat, A.; Guglielmetti, R.; Olieveira-Campos, A. F. M. *Helv. Chim. Acta* **2001**, *84*, 1163. (e) Olivera, M. M.; Salvador, M. A.; Coelho, P.; Carvalho, L. M. *Tetrahedron* **2005**, *61*, 1681. (f) Hepworth, J. D.; Heron, B. M. In *Progress in Heterocyclic Chemistry*; Gribble, G. W., Joule, J., Eds.; Elsevier Science: New York, 2005: Vol 17, p 33.

(7) (a) Rathore, R.; Burns, C. L.; Deselnicu, M. I. *Org. Lett.* **2001**, *3*, 2887. (b) Rathore, R.; Burns, C. L. *J. Org. Chem.* **2003**, *68*, 4071. (c) Rathore, R.; Burns, C. L.; Guzei, I. A. *J. Org. Chem.* **2004**, *69*, 1524. (d) Vyas, V. S.; Rathore, R. *Chem. Commun.* **2010**, *46*, 1065. (e) Zhai, L.; Shukla, R.; Rathore, R. *Org. Lett.* **2009**, *11*, 3474. (f) Wolf, R.; Ghavtadze, N.; Weber, K.; Schnockelborg, E. M.; de Bruin, B.; Ehlers, A. W.; Lammertsma, K. *Dalton Trans.* **2010**, *39*, 1453. (g) Endo, A.; Adachi, C. *Jpn. J. Appl. Phys.* **2010**, *49*, 050205(1−3). (h) Garcia, L. J.; Kaltbeitzel, A.; Pisula, W.; Gutmann, J. S.; Klapper, M.; Mullen, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 9951. (i) Matsumura, S.; Hlil, A. R.; Al-Souz, M. A. K.; Gaudet, J.; Guay, D.; Hay, A. S. *J. Polym. Sci: Part A: Polym. Chem.* **2009**, *47*, 5461. (j) Duarte, T. M. F.; Gegout, A.; Olivier, J.; Cardinali, F.; Nierengarten, J. F. *Eur. J. Org. Chem.* **2009**, 3879. (k) Terazono, Y.; Kodis, G.; Liddell, P. A.; Garg, V.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Phys. Chem. B.* **2009**, *113*, 7147.

(8) (a) Zhi, L.; Wu, J.; Mullen, K. *Org. Lett.* **2005**, *7*, 5761. (b) Mossinger, D.; Hornung, J.; Lei, S.; Feyter, S. D.; Hoger, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 6802. (c) Terazono, Y.; Kodis, G.; Liddell, P. A.; Garg, V.; Gervaldo, M.; Moore, T. A.; Moore, A. L.; Gust, D. *Photochem. Photobiol.* **2007**, *83*, 464. (d) Maly, K. E.; Gagnon, E.; Maris, T.; Wuest, J. D. *J. Am. Chem. Soc.* **2007**, *129*, 4306. (e) Potter, R. G.; Hughes, T. S. *Org. Lett.* **2007**, *9*, 1187. (f) Nijegorodov, N.; Zvolinsky, V.; Luhanga, P. V. C. *J. Photochem. Photobiol. A* **2008**, *196*, 219. (g) Zheng, Q.; Ohulchanskyy, T. Y.; Sahoo, Y.; Prasad, P. N. *J. Phys. Chem. C* **2007**, *111*, 16846.

(9) Sun, D.; Rosokha, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5133.

(10) (a) Lambert, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 7337. (b) Lambert, C.; Noll, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 2107. (c) Heckmann, A.; Lambert, C.; Goebel, M.; Wortmann, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 5851.

(11) For analogous σ-delocalization in hexaiodobenzene dicataion, see: Sagl, D. J.; Martin, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 5827.

(12) (a) Watanabe, S.; Kido, J. *Chem. Lett.* **2007**, *36*, 590. (b) Thomas, K. R. J.; Velusamy, M.; Lin, J. T.; Chuen, C. H.; Tao, Y. T. *J. Mater. Chem.* **2005**, *15*, 4453. (c) Li, Z.; Ye, S.; Liu, Y.; Yu, G.; Wu, W.; Qin, J.; Li, Z. *J. Phys. Chem. B* **2010**, *114*, 9101.

(13) (a) Mossinger, D.; Chaudhuri, D.; Kudernac, T.; Lei, S.; Feyter, S. D.; Lupton, J. M.; Hoger, S. *J. Am. Chem. Soc.* **2010**, *132*, 1410. (b) Lei, S.; Heyen, A. V.; Feyter, S. D.; Surin, M.; Lazzaroni, R.; Sabine Rosenfeldt, S.; Ballauff, M.; Lindner, P.; Mossinger, D.; Hoger, S. *Chem.—Eur. J.* **2009**, *15*, 2518.

(14) Keirstead, A. E.; Bridgewater, J. W.; Terazono, Y.; Kodis, G.; Straight, S.; Liddell, P. A.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2010**, *132*, 6588.

(15) Matsumura, S.; Hlil, A. R.; Lepiller, C.; Gaudet, J.; Guay, D.; Hay, A. S. *Macromolecules* **2008**, *41*, 277.

(16) (a) Yoshida, H.; Watanabe, M.; Fukushima, H.; Ohshita, J.; Kunai, A. *Org. Lett.* **2004**, *6*, 4049. (b) Segura, J. L.; Martin, N. *Chem. Rev.* **1999**, *99*, 3199. (c) Van De Water, R. W.; Pettus, T. R. R. *Tetrahedron* **2002**, *58*, 5367.

(17) (a) Kodama, Y.; Nakabayashi, T.; Segawa, K.; Hattori, E.; Sakuragi, M.; Nishi, N.; Sakuragi, H. *J. Phys. Chem. A* **2000**, *104*, 11478. (b) Hobley, J.; Malatesta, V.; Hatanaka, K.; Kajimoto, S.; Williams, S. L.; Fukumura, H. *Phys. Chem. Chem. Phys.* **2002**, *4*, 180.

(18) (a) Moine, B.; Buntinx, G.; Poizat, O.; Rehault, J.; Moustrou, C.; Samat, A. *J. Phys. Org. Chem.* **2007**, *20*, 936. (b) Coelho, P. J.; Carvalho, L. M.; Abrantes, S.; Oliveira, M. M.; Oliveira-Campos, A. M. F.; Samat, A.; Guglielmetti, R. *Tetrahedron* **2002**, *58*, 9505.

(19) (a) Day, P. N.; Wang, Z.; Pachter, R. *J. Phys. Chem.* **1995**, *99*, 9730. (b) Jacquemin, D.; Perpete, E. A.; Maurel, F.; Perrier, A. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13144.

(20) (a) Delbaere, S.; Micheau, J. C.; Vermeersch, G. *J. Org. Chem.* **2003**, *68*, 8968. (b) Delbaere, S.; Houze, B. L.; Bochu, C.; Teral, Y.; Campredon, M.; Vermeersch, G. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1153. (c) Delbaere, S.; Micheau, J. C.; Frigoli, M.; Mehl, G. H.; Vermeersch, G. *J. Phys. Org. Chem.* **2007**, *20*, 929.

(21) (a) Wasserfallen, D.; Mattersteig, G.; Enkelmann, V.; Mullen, K. *Tetrahedron* **2006**, *62*, 5417. (b) Baner, R. E.; Enkelmann, V.; Wiesler, U. M.; Berresheim, A. J.; Mullen, K. *Chem. —Eur. J.* **2002**, *8*, 3858. (c) Bart, J. C. J. *Acta Crystallogr., Sect. B:Struct. Crystallogr. Cryst. Chem.* **1968**, *24*, 1277. (d) Ning, G. L.; Liu, C. H.; Qu, P.; Zhang, S. W.; Lin, Y.; Munakata, M. *Acta Chim. Sin.* **2000**, *58*, 1095. (e) Larson, E. M.; Von Dreele, R. B.; Hanson, P.; Gust, J. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *46*, 784. (f) Muller, M.; Iyer, V. S.; Kubel, C.; Enkelmann, V.; Mullen, K. *Angew. Chem., Int. Ed.* **1997**, *36*, 1607. (g) Bernhardt, S.; Kastler, M.; Enkelmann, V.; Baumgarten, M.; Mullen, K. *Chem.—Eur. J.* **2006**, *12*, 6117. (h) Tong, L.; Lau, H.; Ho, D. M.; Junior, R. A. P. *J. Am. Chem. Soc.* **1998**, *120*, 6000.

(22) (a) Caelho, P. J.; Carvalho, L. M.; Rodrigues, S.; Oliveira-Campos, A. M. F.; Dubest, R.; Aubard, J.; Samat, A.; Guglielmetti, R. *Tetrahedron* **2002**, *58*, 925. (b) Martins, C. I.; Coelho, P. J.; Carvalho, L. M.; Oliveira-Campos, A. M. F.; Samat, A.; Guglielmetti, R. *Helv. Chim. Acta* **2003**, *86*, 570. (c) Favaro, G.; Ortica, F.; Romani, A. *New J. Chem.* **2003**, *27*, 639. (d) Favaro, G.; Ortica, F.; Romani, A.; Kish, D.; Blackburn, F. *New J. Chem.* **2005**, *29*, 977.

(23) For control of rate and reaction quantum yields of a photochromic system based on stabilization of the excited state via localization of the excitation of energy in pyrene, see: Miyasaka, H.; Satoh, Y.; Ishibashi, Y.; Ito, S.; Nagasawa, Y.; Taniguchi, S.; Chosrowjan, H.; Mataga, N.; Kato, D.; Kikuchi, A.; Abe, J. *J. Am. Chem. Soc.* **2009**, *131*, 7256.

(24) Zhao, W.; Carreira, E. M. *Org. Lett.* **2003**, *5*, 4153.

(25) Adjabeng, G.; Brenstrum, T.; Frampton, C. S.; Roberton, A. J.; Hillhouse, J.; McNulty, J.; Capretta, A. *J. Org. Chem.* **2004**, *69*, 5082.

(26) Urgaonkar, S.; Verkade, J. G. *J. Org. Chem.* **2004**, *69*, 5752.

(27) Yue, D.; Yao, T.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 10292.