Contrasting Photochromic and Acidochromic Behaviors of Pyridyl- and Pyrimidylethynylated Mono- and Bis-Benzopyrans

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ABSTRACT: Investigation of photochromic and acidochromic behaviors of a set of pyridyl- and pyrimidylethynylated mono- and bis-benzopyrans reveals an intriguing influence of the N-heteroaryl ring on spectrokinetic properties of the photogenerated o-quinonoid colored reactive intermediates. While the absorption maxima of the pyrimidylethynylated bis-benzopyran and its photogenerated o-quinonoid colored species undergo bathochromic shifts by ca. 40 and 22 nm, respectively, in the presence of an acid (e.g., trifluoroacetic acid (TFA)), the same remain unaffected for the analogous pyridylethynylated bis-benzopyran and its photogenerated o-quinonoid colored species under similar conditions. Modification of the photochromic behavior of these benzopyrans and, hence, spectrokinetic properties of their photogenerated o-quinonoid species in the presence of H⁺ is a consequence of relative proton affinities of N-heteroaryl rings, i.e., pyridyl/pyrimidyl, and the resonance effects relayed through the ethynyl spacers in a push–pull π-delocalized-type skeleton; the mesomeric effects operate in a contrasting manner depending on the N-heteroaryl ring in the absence and in the presence of an acid. These molecular systems offer a unique opportunity to modulate both photochromic and acidochromic properties of benzopyrans and their photogenerated colored o-quinonoid intermediates by leveraging N-heteroaromatic rings.

INTRODUCTION

Stimuli-responsive materials form the kernel of cutting-edge research on molecular switches, nanoscale machines, sensors, molecular electronic devices, polymers, gels, etc. owing to potential functional applications. In particular, design and synthesis of molecular systems that respond to photon as an external stimulus constitute important endeavors in the development of photochromic materials, which are of significant contemporary interest not only for their practical applications, e.g., in variable transmission glasses, imaging devices, smart windows, etc., but also for opportunities that they offer in controlling several biological phenomena. Photochromism of molecular systems based on spiropyrans, vinylethynedi-naphthofurans, indolinoaxazolidines, etc., can be coupled to acidochromism (acid/base as the external stimulus) to develop multistimuli-responsive materials for applications in digital signal communications. Among several photochromic systems, diarylenzo-/naphthopyrans are of particular importance from the point of view of emerging applications in the development of ophthalmic lenses and functional materials. Photoirradiation of diarylenzoypyrans (closed forms) leads to C(sp²)=O bond heterolysis in their singlet excited states, resulting in the formation of colored o-quinonoid reactive intermediates (open forms), which thermally revert to initial ring-closed forms (T-type photochromism, Figure 1). The parent 2,2-diphenyl-2H-1-benzopyran without any structural modification is known to exhibit photochromism only at very low temperatures (ca. 173 K) due to the extremely fast thermal reversion of the photogenerated o-quinonoid intermediate at room temperature. Thus, modulation of the spectrokinetic properties of o-quinonoid reactive intermediates and the associated photochromic phenomenon of diarylenzoypyrans have been a subject of extensive investigations.

We have, for some time, been interested in the chemistry of photochromic diarylenzo-/naphthopyrans. We have explored the influence of various factors, e.g., electronic effects transmitted by arylation, toroidal conjugation, through-space interaction, helicity as a steric force, etc., on the persistence of o-quinonoid colored reactive intermediates that are generated by photolysis of diarylenzoypyrazins. Compelling results from our recent studies have shown that strong mesomeric effects transmitted by arylenethynylation influence spectral as well as kinetic behavior of the photogenerated colored o-quinonoid reactive intermediates to permit their observation at room temperature. Unlike in arylated...
diphenylbenzopyrans, the ethynyl spacer completely offsets steric inhibition of resonance in addition to bringing about a bathochromic shift in the absorptions and modifying the lifetimes of the photogenerated colored intermediates. In the course of one of our recent investigations, we exploited metal-mediated self-assembly of programmed photochromic organic linkers based on arylethynylated diphenylbenzopyrans with bulged cores to develop photoresponsive two-dimensional metal–organic framework nanosheets for functional applications. During these investigations, we were spurred to explore the photochromic behavior of a set of pyridyl- and pyrimidylethynylated bis- and mono-benzopyrans (Py-/Pm-BBP), as shown in Figure 1.

Our premise for consideration of these molecular systems was that the mesomeric effect between pyran oxygen and aryl nitrogen via push–pull π-delocalization should operate differently.
ently for pyridyl and pyrimidyl moieties as chronicled in Scheme 1. We envisaged that the relative proton affinities (i.e., basicities) of the pyridine/pyrimidine nitrogen(s) may influence mesomeric effects differently, whereby the molecular systems may typically behave as classical donor–π–acceptor (D–π–A) systems with different degrees of delocalization, vide infra.44–49 Contrasting absorption features were expected for the analogous pyridyl- and pyrimidylethynylated benzopyrans along with interesting spectrokinetic properties for their photogenerated colored o-quinonoid reactive intermediates. These systems were thus expected to offer opportunities for combining photochromic behavior with acidochromic properties. Herein, we report that pyridyl- (Py-BBP) and pyrimidylethynylated (Pm-BBP) bis-benzopyrans exhibit divergent photochromic behaviors under acidic conditions such that the spectrokinetic properties of their respective o-quinonoid colored reactive species can be modulated by leveraging resonance effects in the form of π-delocalization.

**RESULTS AND DISCUSSION**

**Synthesis and Single-Crystal X-ray Structure Determination of BBPs and MBPs.** The synthetic protocols for target bis- (BBPs) and mono-benzopyrans (MBPs) are shown in Scheme 2. To begin with, 2,5-diiodobenzene-1,4-diol (1) and 2,5-diiodo-4-methoxyphenol (2) were subjected to cyclocondensation with 1,1-diphenylpropargyl alcohol in the presence of a catalytic amount of acid (PTSA), leading to the diiodo-substituted benzopyrans BBP and MBP, respectively, according to the procedure reported by us earlier.13 Subsequently, the resultant diiodo-substituted benzopyrans...
BBP and MBP were subjected to Sonogashira/“sila”-Sonogashira cross-coupling reactions with appropriate ethynylated arenes under Pd-catalyzed conditions to afford the requisite pyridyl-/pyrimidylenethylated target compounds in excellent isolated yields. Py-BBP was available from our earlier investigation.45

Single crystals of suitable quality were successfully grown for the benzopyrans Py-BBP, Pm-BBP, Py-MBP, and Pm-MBP by slow evaporation of their solutions in CHCl₃ at room temperature and were subjected to X-ray structure determinations (Tables S1 and S2 and Figures S1–S4). The diffraction intensity data collection and subsequent refinements reveal that the crystals belong to the triclinic and monoclinic systems. In Figure 2 are shown perspective drawings of their molecular structures, which reveal that (i) the pyridine and pyrimidine rings—linked to the benzopyran moiety via the ethynyl spacers—are almost coplanar with the benzene ring of the benzopyran nucleus (the dihedral angle varies between ca. 5.8 and 9.2° in all cases), and (ii) the pyran moiety is considerably twisted with respect to the benzene ring.

Photochromic and Acidochromic Behaviors of BBPs and MBPs. The photo- and acidochromic properties of all the benzopyrans were investigated for their dilute solutions in CHCl₃ (50 μM) for their yellow solutions at 298 K in the cases of Py-/Pm-BBP and 263 K in the cases of Py-/Pm-MBP and Ph-BBP. The absorption spectra for the yellow solutions of all of the benzopyrans taper off within 2 min as compared to those observed for analogous mono-benzopyrans Py-MBP and Pm-BBP are found to be bathochromically shifted by ca. 30 nm as compared to those observed for analogous mono-benzopyrans Py-MBP and Pm-MBP (Table 1). Upon photoirradiation (λₑₓc = 350 nm), the yellow solutions of the benzopyrans were found to undergo ready green coloration (at 298 K in the cases of Py-/Pm-BBP and at 263 K in the cases of Py-/Pm-MBP) with the appearance of broad bands in the visible region that extend up to ca. 850 nm (Figures 3, S8 and S9). It is noteworthy that the photogenerated colored species of the mono- and bis-benzopyran systems exhibit almost similar absorption maxima that vary between ca. 610 and 620 nm.

The photogenerated green-colored intermediates of the benzopyrans were found to revert to the original yellow forms within 2–3 min on standing in the dark at room temperature. The thermal bleaching kinetics of the colored species were recorded at 298 K. The thermal decay for the colored intermediates were monitored after steady-state photolysis of their acidified solutions, respectively. Note the color changes (in the insets) attendant upon photoirradiation and acidification.

![Figure 3](https://doi.org/10.1021/acsomega.1c02948)

**Figure 3.** UV–vis absorption spectra (50 μM in CHCl₃) of Py-BBP (left) and Pm-BBP (right) before (black line) and after steady-state photoirradiation (green line). The red and blue lines designate the absorption spectra of the benzopyrans acidified with 4 mM TFA and photolyzates of their acidified solutions, respectively. Note the color changes (in the insets) attendant upon photoirradiation and acidification.

|-Benzopyran | Condition | ε (nm) (M⁻¹ cm⁻¹) | k₁ (s⁻¹) | k₂ (s⁻¹) |
|-----------|-----------|------------------|----------|----------|
| Py-BBP    | without TFA | 430 (9000) 608 | 0.006, 0.0023 |
|           | with TFA   | 470 630         | 0.012, 0.005 |
| Pm-BBP    | without TFA | 430 (8500) 608 | 0.004, 0.0015 |
|           | with TFA   | 430 608         | 0.006, 0.002 |
| Py-MBP    | without TFA | 400 (12500) 610 | 0.032, 0.012 |
|           | with TFA   | 435 – “       | “       |
| Pm-MBP    | without TFA | 400 (12000) 610 | 0.012, 0.0046 |
|           | with TFA   | 400 – “       | “       |
| Ph-BBP    | without TFA | 420 (9200) 618 | 0.013, 0.0051 |
|           | with TFA   | 420 618        | 0.017, 0.0066 |

*Based on absorption spectra of the chloroform solutions (50 μM) of the benzopyrans without and in the presence of 4 mM trifluoroacetic acid (TFA); the error in determination of molar extinction coefficients (ε in M⁻¹ cm⁻¹) was ± 2%. The thermal decay for the colored intermediates were monitored after steady-state photo-irradiation (λₑₓc = 350 nm) of the pyran solutions for 3–5 min. The amplitudes (%) of the fast (k₁) and slow (k₂) decaying components in each case were 75 and 25%, respectively. The spectrokinetic properties of the photogenerated colored species were recorded at 298 K. The spectrokinetic properties of the photogenerated colored species were recorded at 263 K. The thermal decay was too fast to preclude monitoring of the spectrokinetic properties of the colored species even at 233 K.

in the cases of Py-/Pm-BBP and at 263 K in the cases of Py-/Pm-MBP (Table 1). Of course, the duration of photo-irradiation required for reaching the photostationary state (PSS) was evaluated from coloration plots (Figure S13). The absorption decay of the colored species even at 233 K.

**Table 1.** Absorption Properties and Spectrokinetic Data of Various Benzopyrans and Their Respective Photogenerated Colored Intermediates
slower decay rates \( \left( k_1 \right) \) when compared to those of their mono-benzopyran analogues, i.e., Py-MBP and Pm-MBP, and (ii) the decay rates \( \left( k_2 \right) \) are comparatively faster for the colored species of the pyridylethynylated benzopyrans (Py-BBP and Py-MBP) than those of the pyrimidylethynylated analogues (Pm-BBP and Pm-MBP). This signifies considerable influence of the N-heteroaryl ring (i.e., pyridyl/pyrimidyl) that is installed at 5 and 8 positions of the benzopyran moiety through ethynyl spacers on the spectrokinetic properties of the photogenerated colored intermediates. Notably, to examine the fatigue resistance of these benzopyrans to photoirradiation, several coloration-reversion photochromic cycles were carried out (Figures S14–S16). These experiments did not reveal any indication of photodegradation of benzopyrans, which attests to the robustness of the molecular systems.

Insofar as the acidochromic behavior is concerned, the optical properties of benzopyrans in the presence of a strong acid such as TFA were found to be rather intriguing with a contrasting difference for the pyridine- and pyrimidine-substituted analogues. The long-wavelength absorption maximum of Py-BBP (430 nm) was found to undergo a progressive bathochromic shift (by ca. 40 nm) to 470 nm with addition of increasing concentrations of TFA up to ca. 80 molar equivalents with the color changing readily from yellow to orange (Figures 3 and 4). Similarly, the absorption maximum of Py-MBP (400 nm) was also found to bathochromically shift (ca. 35 nm) to 435 nm in the presence of TFA although the yellow color of the solution remained the same in this case (Figure S8).

In stark contrast, the absorption features as well as the yellow color of the pyrimidylethynylated benzopyrans, i.e., Pm-BBP and Pm-MBP, were not found to be affected upon acidification under similar conditions (Figures 3, 4, and S9). In other words, between Py-BBP and Pm-BBP, only the former exhibits acidochromic behavior. It should be noted, in this regard, that while Py-BBP/Py-MBP exhibits acidochromic behavior in the presence of TFA, such acidochromic behavior was not evidenced whatsoever in the presence of a weaker acid such as acetic acid (Figure S7).

In a similar manner, the spectrokinetic properties of the colored intermediates of all benzopyrans were found to be remarkably influenced by the addition of TFA. The latter manifested in significant enhancement of thermal decay rates such that the formation of the colored species from the acidified solutions of the benzopyrans was observed only at low temperatures, e.g., at 263 K instead of 298 K for the same in the absence of any acid (Table 1 and Figure 5). In fact, the thermal reversion was found to be too fast even at 233 K to preclude monitoring of the spectrokinetic properties of the colored species of the mono-benzopyrans, i.e., Py-MBP and Pm-MBP, in the presence of TFA (Table 1). Notably, solution-state photolysis of Py-BBP in the absence and in the presence of TFA (ca. 80 molar equivalents) led to the formation of green-colored species in both cases but with their absorption maxima located at 608 and 630 nm, respectively (Figure 3 and Table 1). In other words, the absorption maximum of the photogenerated green-colored species of Py-BBP undergoes a bathochromic shift of ca. 22 nm in the presence of H\. In contrast, the green-colored species obtained upon photolysis of Pm-BBP in the absence and in the presence of TFA exhibited no discernible change in the absorption maximum (608 nm) (Figure 3 and Table 1). These observations clearly attest to the remarkable influence of an acid on the spectrokinetic properties of N-heteroarylethynylated benzopyrans, more importantly, their photogenerated colored species.

To further elucidate the contrasting difference in spectrokinetic behaviors of pyridyl- (Py-BBP) and pyrimidylethynylated bis-benzopyrans (Pm-BBP) in the presence of an acid, we examined photo- and acidochromic properties of the phenylethynylated bis-benzopyran Ph-BBP, a system that is devoid of any nitrogen atom (Figure 1). Interestingly, the absorption spectral pattern of Ph-BBP was found to be akin to that of Pm-BBP in that the absorption maximum of the former maximum of Py-MBP (400 nm) was also found to bathochromically shift (ca. 35 nm) to 435 nm in the presence of TFA although the yellow color of the solution remained the same in this case (Figure S8). In stark contrast, the absorption features as well as the yellow color of the pyrimidylethynylated benzopyrans, i.e., Pm-BBP and Pm-MBP, were not found to be affected upon acidification under similar conditions (Figures 3, 4, and S9). In other words, between Py-BBP and Pm-BBP, only the former exhibits acidochromic behavior. It should be noted, in this regard, that while Py-BBP/Py-MBP exhibits acidochromic behavior in the presence of TFA, such acidochromic behavior was not evidenced whatsoever in the presence of a weaker acid such as acetic acid (Figure S7).

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(420 nm) and its photogenerated colored species (618 nm) remained the same in the absence and presence of TFA (Table 1 and Figure S11). However, like in all other cases, the thermal decay rate of the colored species of Ph-BBP was found to increase in the presence of TFA (Table 1 and Figure S12). Further, the acidochromic properties of Py-BBP and Py-MBP in the presence of TFA were found to exhibit an acid/base reversible behavior; the acidified forms of Py-BBP/Py-MBP could be easily neutralized by addition of a base such as K₂CO₃, validated by UV–vis absorption spectral changes (Figure S17).

Figure 6. ¹H NMR (400 MHz) spectra of Py-BBP (0.03 M in CDCl₃) in the presence of 0 (a), 20 (b), 40 (c), 60 (d), and 80 (e) molar equivalents of TFA at 298 K. Notice the change of color from yellow (a) to orange (e) upon addition of TFA.

Contrasting Spectrokinetic Behavior of Py-/Pm-BBP and Their Photogenerated Colored Intermediates under Acidic Conditions. Mechanistic details of the photochromic properties of benzopyrans have been extensively investigated.⁵⁻¹⁰ Needless to mention that the TC and TT isomeric forms of the o-quinonoid reactive intermediates shown in Figure 1 are mainly responsible for the observed coloration attendant upon photoirradiation of benzopyrans. The TT isomer is generated by a two-photon absorption of the benzopyran through initial formation of the TC isomer such that the former is likely to be formed only minimally when the precursor benzopyran is subjected to photoirradiation for a shorter duration. Thus, at shorter durations of irradiation, it is the TC isomer that is largely responsible for the observed color. The parent 2,2-diphenyl-2H-1-benzopyran is known to exhibit photochromism at a very low temperature (ca. 173 K) due to the extremely fast reversion of the o-quinonoid reactive intermediates at room temperature with slow thermal decay rates. Notably, the photogenerated colored species of the BBPs and MBPs exhibit almost similar absorption maxima, which vary between ca. 610 and 620 nm. This is suggestive of ring-opening of only one benzopyran moiety. The relative contributions from the fast-decaying TC (major) and slow-decaying TT (minor) isomers of the o-quinonoid reactive species in all cases are found to be ca. 75% (for k₁) and 25% (for k₂), respectively. In other words, the second pyran moiety in the BBPs merely serves as a substituent, just as the methoxy substituent in the case of the MBPs, and accounts for the unremarkable difference observed. The absorption maxima of BBPs (430 nm) are found to be bathochromically shifted by ca. 30 nm when compared to those of MBPs (400 nm) due to the presence of an additional C=O as part of the extra pyran ring.

Let us now consider the behavior of the pyridyl- (Py-BBP) and pyrimidylethynylated (Pm-BBP) bis-benzopyrans and their photogenerated o-quinonoid reactive intermediates under acidic conditions (i.e., 80 molar equivalents of TFA). As mentioned earlier, between Py-BBP and Pm-BBP, only the former lends itself to acidochromism. While the yellow solution (λ_max ca. 430 nm) of Py-BBP readily changes to orange (λ_max ca. 470 nm) in the presence of TFA (80 molar equivalents), that of Pm-BBP was found to remain the same (λ_max ca. 430 nm). Similarly, the green-colored o-quinonoid reactive species photogenerated from Py-BBP exhibits an absorption maximum at 608 nm, which undergoes a bathochromic shift (by ca. 22 nm) to 630 nm in the presence of TFA. In contrast, the green o-quinonoid reactive species photogenerated from Pm-BBP exhibited no discernible change
in the absorption maximum ($\lambda_{\text{max}} = 608$ nm) in the absence and in the presence of TFA. Such a contrasting difference in the absorption properties of analogous bis-benzopyrans and their photogenerated $\pi$-quinonoid reactive species in the presence of an acid should be attributed to relative proton affinities of the nitrogen-containing aryl rings, i.e., pyridine (in the case of Py-BBP) and pyrimidine (in the case of Pm-BBP). Seemingly, the $pK_a$ values of the conjugate acids of pyridine and pyrimidine, i.e., protonated pyridinium and protonated pyrimidinium cations, are ca. 5.2 and 1.1, respectively. Evidently, pyridine has a significantly higher proton affinity than that of pyrimidine, the weaker basicity of pyrimidine as compared to that of pyridine is known to originate from the presence of the second nitrogen atom (sp$^3$ hybridized) at the metaposition of pyrimidine. As is evident from the UV–vis absorption spectra, the highly basic nitrogen atoms of the pyridine rings in Py-BBP should be protonated in the presence of a strong acid, i.e., TFA, in contrast to the weakly basic nitrogen atoms of the pyrimidine rings in Pm-BBP.

To gain structural insights to substantiate the influence of $H^+$ on the absorption spectrum and color change of Py-BBP, we recorded the $^1$H NMR spectra of the latter (0.03 M in CDCl$_3$) in the presence of increasing concentrations of TFA up to 80 molar equivalents (Figure 6). Accordingly, one notices that (i) the doublets corresponding to the protons of the pyridyl ring at 7.38 and 8.61 ppm undergo significant downfield shift to 7.83 and 8.80 ppm, respectively; (ii) the doublets corresponding to two olefinic protons of the pyran ring at 6.40 and 7.01 ppm undergo marginal downfield and upfield shift to 6.46 and 6.95 ppm, respectively; and (iii) the $^1$H NMR signals for the phenyl rings at the C2 position of the benzopyran moiety (7.24–7.52 ppm) come closer to each other with increasing concentration of TFA. Notably these changes in the proton resonances of Py-BBP are also accompanied by a color change of the solution from yellow to orange in the presence of TFA (Figure 6). Therefore, the changes revealed by UV–vis absorption spectra and $^1$H NMR titration experiments suggest that the pyridyl nitrogens of Py-BBP undergo protonation in the presence of TFA.

To unequivocally establish the fact that both of the pyridyl nitrogens of Py-BBP undergo protonation, we got hold of the single crystals of the trifluoroacetate salt of Py-BBP suitable for X-ray structure determination (Table S3 and Figure S5). The orange crystals of suitable quality were successfully grown by slow evaporation of the CHCl$_3$ solution of Py-BBP saturated with TFA (80 molar equivalents). The asymmetric unit of the crystal structure consists of one-half of the molecule with a pyridinium cation, a trifluoroacetate anion, and a guest trifluoroacetic acid molecule (Figures 7 and S5). Therefore, given that both nitrogens of Py-BBP undergo protonation in the presence of excess TFA, it should be fair to assume that the protonation should also hold true in the case of the photogenerated colored $\pi$-quinonoid reactive intermediates photogenerated from Py-BBP.

Based on the observed changes as reflected by UV–vis absorption spectra, $^1$H NMR titration, and X-ray crystal structure analysis, we may now rationalize structural aspects that account for the photobehavior of Py-BBP in the presence of TFA. As shown in Scheme 3, in the case of Py-BBP, one may envisage the operation of mesomeric effect from one of the pyran oxygens to one of the pyridine nitrogens such that the molecule typically behaves like a push–pull donor–$\pi$–acceptor ($D$–$\pi$–$A$) system. Such a resonance via $\pi$-delocalization in STATE-A (yellow; $\lambda_{\text{max}} = 430$ nm) should become more meaningful when the two pyridine nitrogens get protonated and become more electron-deficient in STATE-B (orange; $\lambda_{\text{max}} = 470$ nm). Notably, such resonance effects are anticipated to be relayed through the ethynyl spacers without any steric inhibition of electronic conjugation. This is evident from the fact that the pyridine rings linked to the benzopyran moiety via the ethynyl spacer are almost coplanar with the benzene ring of the benzopyran nucleus as revealed by X-ray crystal structure analysis, vide supra. By the same token, the influence of $H^+$ on the spectrokinetic properties of the colored $\pi$-quinonoid reactive intermediates (STATE-C and STATE-D, Scheme 3) is also glaring. For example, photolysis of the yellow solution of Py-BBP in the absence of TFA (STATE-A) leads to the green-colored species with $\lambda_{\text{max}}$ at 608 nm (STATE-C), which gets bathochromically shifted to 630 nm upon addition of TFA (STATE-D). Furthermore, acidification of the yellow solution of Py-BBP led to its protonated form with an orange color (STATE-B), photolysis of which resulted in the formation of the same green species with $\lambda_{\text{max}}$ at 630 nm (STATE-D) instead of 608 nm (STATE-C). The bathochromic shift of ca. 22 nm in the absorption maximum of STATE-D when compared to that of STATE-C is evidently a consequence of the strong resonance effect operative in the form of $\pi$-delocalization between the pyran oxygen and the pyridinium nitrogen in case of the former. In stark contrast, due to the absence of such resonance effects (i.e., push–pull $\pi$-delocalization) and due to the weak proton affinity of the pyrimidine nitrogens, only negative inductive effects of the neutral pyrimidyl moieties are expected to operate on the pyran oxygens in Pm-BBP. Therefore, it should be reasonable to assume that Pm-BBP and its photogenerated $\pi$-quinonoid
reactive species exist as neutral species in the form of STATE-A (instead of STATE-B) and STATE-C (instead of STATE-D), respectively, in both the absence and presence of H⁺. This is in complete agreement with the fact that the absorption maxima of Pm-BBP (430 nm) and its photogenerated o-quinonoid reactive species (608 nm) remain the same in the absence and presence of TFA.
absence and corroborated by a perusal of the photchemoic properties of the phenylethynylated bis-benzopyran Ph-BBP, a system that is devoid of any N-heterocyclic ring, vide supra. As mentioned earlier, the photochromic behavior of Ph-BBP is found to be similar to that of Pm-BBP in that the absorption maxima of the former (420 nm) and its photogenerated colored \(\sigma\)-quinonoid reactive species (618 nm) do not undergo any change whatsoever in the absence and in the presence of TFA. Therefore, while the photochromic behavior of Py-BBP can be perturbed in the presence of TFA, such a change is precluded in the case of Pm-/Ph-BBP. Therefore, these molecular systems offer a unique opportunity to combine photochromic and acidochromic properties, whereby spectrokinetic parameters of the photogenerated colored \(\sigma\)-quinonoid reactive intermediates can be modulated by leveraging relative proton affinities of \(N\)-heteroaryl ring(s) and resonance effects operating through push–pull \(\pi\)-delocalization in \(\pi\)-conjugated skeletons. These results are anticipated to be of much relevance to a gamut of novel photoresponsive functional materials.

**CONCLUSIONS**

A set of photochromic pyridyl- and pyrimidylethynylated bis-(BBPs) and mono-benzopyrans (MBPs) was synthesized by Sonogashira coupling reaction as the key synthetic step. Photoirradiation of the yellow solutions of all benzopyrans leads to instant green coloration. The photogenerated \(\sigma\)-quinonoid colored reactive intermediates of BBPs and MBPs exhibit almost similar absorption maxima that vary between ca. 610 and 620 nm, suggesting the ring-opening of the benzopyran moiety. Thermal reversion kinetics of photogenerated colored species show that comparatively slower decay rates are observed for the colored transients generated from the bis-benzopyrans when compared to their monobenzopyran analogues in that the pyridylethynylated systems are found to exhibit much faster thermal bleaching of their colored intermediates than those of the corresponding pyrimidylethynylated systems. Thus, the \(N\)-heteroaryl ring, i.e., pyridyl/pyrimidyl, that is installed at 5 and 8 positions of the benzopyran moiety through ethynyl spacers exerts considerable influence on the spectrokinetic properties of the photogenerated colored transients. A glaring contrast in the photochromic properties of the pyridyl- (Py-BBP) and pyrimidylethynylated (Pm-BBP) bis-benzopyrans is readily discerned under acidic conditions. While Py-BBP exhibits a bathochromic shift (by ca. 40 nm) of the absorption maximum upon addition of TFA, the absorption features of Pm-BBP were found to remain the same in the presence of TFA. Similarly, while the green-colored \(\sigma\)-quinonoid species photogenerated from Py-BBP exhibits a bathochromic shift (by ca. 22 nm) of the absorption maximum in the presence of TFA, no such spectral change is witnessed for the same in the case of Pm-BBP. These results are rationalized based on the relative proton affinities (i.e., basicities) of the nitrogen atom(s) of the pyridyl/pyrimidyl rings and divergent resonance effects operating over the push–pull conjugated system (i.e., donor–\(\pi\)-acceptor) between the pyran oxygen(s) and the aryl nitrogen(s), relayed through the ethynyl spacers. Overall, the results show that simple pyridyl-/pyrimidylethynylation of halogenated mono- and bis-benzopyrans permits access to a series of photochromic molecular systems with tunable spectrokinetic properties of their photogenerated colored \(\sigma\)-quinonoid reactive intermediates and that the latter offer unique opportunity to associate the photochromic properties with acidochromic properties. The results described herein are expected to open up new avenues to develop photoresponsive organic materials with tunable spectrokinetic properties in particular and to multistimuli-responsive functional materials in general.

**EXPERIMENTAL SECTION**

**General Aspects.** All of the reagents employed were available from commercial sources and were used without further purification. Substrates such as 4-(trimethylsilyl)pyridine \(^4\) and 4-(trimethylsilyl)pyrimidine \(^4\) were synthesized according to the procedure reported in the literature. Starting precursors and some of the final products, namely, 2,5-diiodobenzene-1,4-diol (1), 2,5-diiodo-4-methoxyphenol (2), 5,10-diiodo-2,2,7,7-tetraphenyl-2,7-dihydropyrano[2,3-g]chromene (BBP), 5,8-diiodo-6-methoxy-2,2-diphenyl-2H-chromene (MBP), 4,4’-(2,2,7,7-tetraphenyl-2,7-dihydropyrano[2,3-g]chromene-5,10-diyli)(ethylene-2,1-diyli) dipyrindine (Py-BBP), etc., were synthesized according to the procedure reported earlier from our laboratories.\(^{43}\) Tetrahydrofuran (THF) and 1,2-dichloroethane (DCE) were distilled freshly over sodium/benzophenone and anhyd Ca\(_2\)H\(_2\), respectively, prior to use. All other solvents used for synthesis and purification were freshly distilled prior to use. Column chromatography was carried out with silica gel of a 100–200 mesh. The melting points were determined with a standard melting point apparatus. IR spectra were recorded on an FT-IR spectrophotometer. \(^1\)H NMR spectra were recorded on 400 and 500 MHz spectrometers. \(^{13}\)C\(^{1}\)H NMR spectra were recorded on 100 and 125 MHz spectrometers with complete proton decoupling. It should be noted that the \(^{13}\)C\(^{1}\)H NMR spectral data of Pm-BBP, Ph-BBP, Py-MBP, and Pm-MBP reveal the fact that the number of signals observed for carbons is far lesser than the total number of carbons present in each of the molecular structures due to chemical equivalence of several carbons that results in merging/overlapping of some of the peaks. High-resolution mass spectra (HRMS) were recorded on an ESI-Q\(^\text{TOF}\) instrument. UV–vis absorption spectra were recorded on a double-beam spectrophotometer. Solution-state photoysis was carried out in a photoreactor fitted with 350 nm UV lamps (8 W, 14 lamps).

**Synthesis and Characterization Data.** The synthetic procedures for accessing the target molecules and their comprehensive characterization data are described below. “Silai”-Sonogashira coupling reactions were carried out according to the procedure reported earlier from our laboratories.\(^{43}\)

\[4,4’-(2,2,7,7-Tetraphenyl-2,7-dihydropyrano[2,3-g]chromene-5,10-diyli)(ethylene-2,1-diyli)]dipyrindine (Pm-BBP). “Silai”-Sonogashira coupling reaction was performed using BBP (1.00 g, 1.35 mmol), 4-(trimethylsilyl)pyrimidine (0.95 g, 5.39 mmol), triethylamine (10 mL), tetrabutyrammonium fluoride trihydrate (1.70 g, 5.39 mmol), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (0.094 g, 0.14 mmol), and CuI (0.027 g, 0.14 mmol) in THF (40 mL) under an inert atmosphere at 60 °C using an oil bath for 12 h. After this period, the reaction mixture was concentrated in vacuo. The crude contents were then dissolved in CHCl\(_3\) (30 mL) and washed with brine, and the organic material was extracted with CHCl\(_3\) (3 mL × 20 mL). Subsequently, the combined organic
extract was dried over anhyd Na2SO4, filtered, and concentrated to dryness under reduced pressure. The crude material was purified by silica gel column chromatography using 30% EtOAc in hexane, affording pure Pm-BBP as a light-yellow solid in 89% yield (0.83 g); mp. 222–224 °C; IR (KBr) cm−1 3059, 3023, 2921, 2922, 1421, 1304, 1284, 1283, 1278, 1266, 1232, 120.9, 119.9, 113.2, 117.1, 109.5, 92.2, 89.8, 88.2, 83.0, 56.3; HRMS (ESI) m/z: [M + H]+ calcd for C48H31N4O2 695.2447; found 695.2455.

\[
\text{7.41 (m, 2H), 7.40 (m, 2H), 7.49 (m, 4H), 7.36–7.32 (m, 4H), 7.30–7.27 (m, 2H), 7.06 (d, J = 10.1 Hz, 1H), 6.85 (s, 1H), 6.49 (d, J = 10.1 Hz, 1H), 3.87 (s, 3H), 13\text{C}(\text{H}) \text{ NMR (CDCl}_3, 125 \text{ MHz}) \delta 159.8, 158.6, 158.5, 157.5, 156.9, 156.8, 154.3, 147.9, 144.1, 132.4, 132.1, 132.0, 131.9, 128.5, 128.4, 128.3, 127.8, 126.6, 124.1, 121.1, 119.9, 119.8, 113.2, 111.7, 109.5, 92.3, 89.8, 88.2, 83.0, 56.3; HRMS (ESI) m/z: [M + H]+ calcd for C48H31N4O2 695.2447; found 695.2455.}
\]

**Single-Crystal X-ray Structure Determinations.** Single crystals of suitable quality were successfully grown for the benzopyrans Py-BBP, Pm-BBP, Py-MBP, and Pm-MBP, by slow evaporation of their solutions in CHCl3 at room temperature and were subjected to X-ray structure determinations. Similarly, single crystals of appropriate quality of the trifluoroacetate salt of Py-BBP were grown by slow evaporation of the CHCl3 solution of Py-BBP saturated with TFA (80 molar equivalents) at room temperature and were subjected to X-ray structure determinations. The X-ray diffraction intensity data collection for the single crystals of the bis- and mono-benzopyrans was carried out using a CCD detector system equipped with a Mo-sealed Siemens ceramic diffraction tube (λ = 0.7107 Å) and a highly oriented graphite monochromator. The diffraction data were collected in a hemisphere mode and processed with Bruker SAINT. Structures were determined with the SHELXL package and refined by the full matrix least-squares method based on F2 using SHELX-2014 and SHELX-2018 programs. The hydrogen atoms were fixed geometrically and were treated as riding on their nonhydrogens; they were refined isotropically, while all nonhydrogens were subjected to anisotropic refinement.

**Solution-State Photolyses.** In a typical experiment, the solutions (50 μM) of photochromic benzopyrans in CHCl3 (in the absence and in the presence of TFA) were taken in 3 cm3 quartz cuvettes equipped with extended arms, and the solutions were thoroughly purged with nitrogen gas with gentle flow for 5–10 min. Subsequently, the solution of each benzopyran was exposed to UV irradiation in a Luchem photoreactor fitted with 350 nm UV lamps (8 watts, 14 lamps) for 3–5 min at 298 or 263 K. Upon exposure to UV irradiation, the yellow solutions of the benzopyrans were found to undergo ready green coloration. The cuvette in each case was removed from the reactor, and the UV–vis absorption spectrum of the photolysate was recorded immediately.

\[
\text{1H NMR Titration of Py-BBP with TFA. In a typical process, the solution (0.5 mL) of Py-BBP in CDCl}_3 (0.03 M) was treated with increasing equivalents of TFA, and the 1H NMR spectra of such solutions were recorded at 298 K. After addition of TFA to the benzopyran solution each time, the UV–vis absorption spectrum of the photolysate was recorded immediately.}
\]

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02948.

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Tables of single-crystal X-ray data, ORTEP diagrams, various UV–vis absorption spectra, coloration plots, details of photostability studies, acid/base reversibility study for acidochromism and $^{1}$H and $^{13}$C{H} NMR spectra of the compounds. CCDC-1552587, 1552588, 1552589, 1552496, and 1552497 contain the supplementary X-ray crystallographic data (PDF).

Py-BBB (CIF)

Py-BBB (CIF)

Py-BBP-TFA (CIF)

Py-MBP_V (CIF)

Pm-MBP_V (CIF)

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Notes

The authors declare no competing financial interest.

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