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Proton Stabilized Photochemically Reversible *E/Z* Isomerization of Spiropyrans

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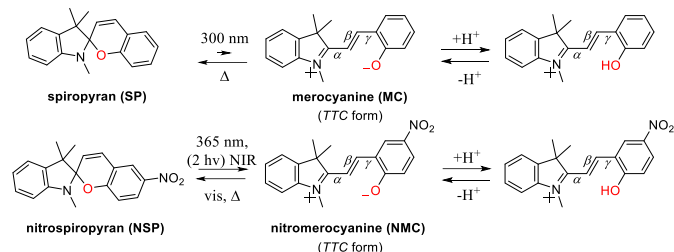
ABSTRACT: Spiropyrans undergo C_{spiro}-O bond breaking to their ring-open protonated E-merocyanine form upon protonation and irradiation via an intermediate protonated Z-merocyanine isomer. We show that the extent of acid induced ring opening is controlled by matching both the concentration and strength of the acid used and with strong acids full ring opening to the Z-merocyanine isomer occurs spontaneously allowing its characterization by ¹H NMR spectroscopy as well as UV/vis spectroscopy, and reversible switching between Z/E isomerization by irradiation with UV and visible light. Under sufficiently acidic conditions both E- and Z-isomers are thermally stable. Judicious choice of acid such that its pK_a lies between that of the E- and Z-merocyanine forms enables thermally stable switching between spiropyran and E-merocyanine forms and hence pH gating between thermally irreversible and reversible photochromic switching.

Introduction

Smart systems built from molecular switches¹ that respond to external triggers such as light,² electricity,³ heat,^{4,5} sound,^{6–8} and pH,⁹ through changes in molecular properties (color, polarity, shape, conductivity, reactivity etc.) are highly desirable due to the possibility to tune these physical responses through structural (synthetic) modification.¹⁰ Building such molecular switches into materials can impart responsiveness at the macroscopic level, often amplifying the changes in physical properties ranging from sensing¹¹ and surface properties¹² to luminescence^{13,14} and electrochromism.^{15,16} Photochromes, including dithienylethenes,^{17,18} azobenzenes^{19,20} and spiropyrans,²¹ are amongst the most widely applied due to their modularity and flexibility towards modification and the possibility to combine them with other responsive units, e.g., multiphotochromes.²² The combination of synthetic versatility, and thermo- and acidochromism shown by spiropyrans in addition to their well-known photochromism reported first in 1952,²³ has made this class amongst the most important in applications in smart materials and systems to date.

The photochromism of spiropyrans arises from a light driven interconversion between a 'ring closed' spiropyran (SP) structure and the zwitterionic 'ring open' merocyanine (MC) state in which the C-O bond of the spiro motif is cleaved, and is stabilized by an accompanying Z/E isomerization around the spiro- and pyran-bridging double bond (**Scheme 1**). The merocyanine 'open form' can

exist as any of several distinct isomers, denoted commonly by reference to the *cis/trans* orientation around each of the three bonds starting at the C_{spiro}-C bond, indicated in Scheme 1 by α, β and γ. The preferred conformations and the complex photochromic pathways for several (neutral) spiropyrans have been studied using various *ab initio* models.^{24–29} The orientation of the β-bond affects the thermal stability of the merocyanine with regard to reversion to the spiropyran form. Although multiple colored isomers have been observed at cryogenic temperatures,³⁰ the low thermal stability of the *cis*-β configurations (referred to as the Z-isomer) means that only the more stable *trans*-β configurations (E-isomer) are observed at ambient temperatures.³¹ Indeed, the TTC form, specifically, was shown by Ernsting and co-workers to be the thermally most stable isomer.³²



Scheme 1. Structures and photochromism of the colorless spiropyran (SP) and nitrospiropyran (NSP). Photo-induced ring-opening can lead to any of 8 distinct isomers differing in conformation, *cis* (C) and *trans* (T), around the α, β and γ bonds. Protonation of the colored merocyanine

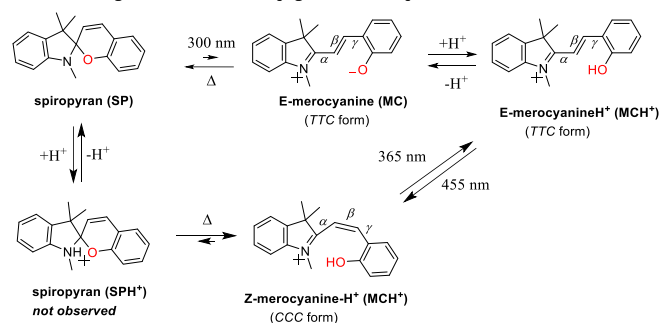
anine form inhibits thermally induced reformation of the spiro form (ring closing).

Protonation of the phenol moiety of the merocyanine form impacts the chemistry of spiropyrans and indeed acidochromism has been reported for several spiropyran structures whereby addition of acid results in thermally induced conversion to the protonated merocyanine form (**MCH⁺**).^{33,34,43–46,35–42} However, the mechanism and nature of the intermediate species formed throughout these reports are not consistent, and several conflicting mechanistic scenarios have been proposed to date.

Both Fissi et al.⁴⁵ and Wojtyk et al.,³³ for example, proposed that a rapid equilibrium between the non-protonated and *N*-protonated spiropyran is established in the presence of trifluoroacetic acid, lying in favor of the protonated *E*-merocyanine form. The immediate conversion the protonated *E*-merocyanine form upon protonation of a spiropyran impregnated polydimethylsiloxane polymer films was noted by Nam and co-workers also, but with subsequent thermal reversion back to the spiropyran form.⁴⁶ Later Genovese et al. reported that reversion to the ring-closed form could be induced by irradiation with visible light also.³⁴ Rémon et al., on the other hand, proposed that, in aqueous media, *N*-protonation only occurs at pH below 0.5, and that the only protonated species present is the ring open merocyanine form which is in thermal equilibrium with the non-protonated closed form.³⁶ Later Schmidt et al. noted the formation of the protonated *E*-merocyanine in ethanol upon addition of trifluoroacetic acid.³⁷ Collectively, these reports indicate that ring opening to the stable protonated *E*-merocyanine occurs upon protonation. However, over two decades ago, Zhou and co-workers reported a species "Y" while investigating the pH dependence of the negative photochromism of a 6',8'-dinitrospiropyran, for which the merocyanine form is most stable even when unprotonated.⁴³ Species Y was assigned to the protonated form of species "X", a transient spiropyran species which has a broken C_{spiro}-O bond and a geometry intermediate to the perpendicular spiro and the planar merocyanine form, and postulated that a rapid equilibrium is established between species Y and the spiro form under sufficiently acidic conditions. In the same period, Roxburgh et al. reported the trifluoroacetic acid induced thermal ring-opening of spiropyrans to their protonated *E* isomer, which was proposed to be via either the unprotonated or protonated *Z* form.⁴⁴ The proposed intermediacy of the protonated *Z* form was supported by Shiozaki subsequently, who proposed that protonation of spiropyran in ethanol with sulfuric acid, a stronger acid than the trifluoroacetic acid, generated the *Z*-merocyanine form, which could not only undergo subsequent thermal but also photochemical *Z/E*-isomerization (**Scheme 2**).³⁸ Shiozaki's interpretation of the changes observed by UV-vis absorption spectroscopy were supported by theoretical studies and is analogous to the acid induced ring opening (C-O bond cleavage) ob-

served for the related photochromic spirooxazines.⁴⁷ The formation of the **Z-MCH⁺** form has been proposed elsewhere as well,⁴⁸ and has been reported in gas-phase studies.⁴⁹

Here, we show through a combination of spectroscopy and theory that the observed pH induced switching of both spiropyrans (**SP**) and nitrospiropyrans (**NSP**) in solution can be rapid and complete (**Scheme 2**) but is highly dependent on acid strength in non-aqueous solvents. The extent of reaction with acids follows the order of *pK_a* values reported, including the intermediate *pK_a* of HNO₃ in the middle, for which an excess amount is required in order to generate the desired response.^{50–52} Furthermore, we show unambiguously that the initial step is cleavage of the C-O bond to form a relatively stable *Z*-isomer of the merocyanine that undergoes thermal as well as photochemically induced *Z/E*-isomerization to the more stable *E*-form. Overall, we show that fully reversible isomerization is retained upon acid/base switching provided that the acid used is stronger than the phenol moiety in at least the *E*-isomer. The demonstration of pH induced switching between spiro and *Z*-merocyanine forms as well as photochemical *E/Z* switching opens new opportunities in the application of spiropyran as molecular switches. It is especially relevant in applications where large local changes in pH can occur such as at electrodes, e.g., during cyclic voltammetry,^{53,54} which can affect the observed photochemistry profoundly.



Scheme 2. pH-gated photochromism of the colorless spiropyran (**SP**). Protonation of **SP** results in spontaneous ring opening to the *Z*-merocyanine (**Z-MCH⁺**). UV irradiation to the thermally stable *E*-merocyanine (**E-MCH⁺**) is reversed by visible irradiation.

It is notable that in most earlier studies of the pH dependence of spiropyran, trifluoroacetic acid^{33–35,37,39,40} as well as HCl,^{21,36,41,42} were the acids of choice employed. Notably, however, in studying pH-gated spiropyran photochromism, Shiozaki employed sulfuric acid.³⁸ Here, we show that the choice of acid is crucial to fully understanding the acido-photochromism of spiropyran. We show that addition of acid to **SP** and **NSP** induces a bathochromic shift, the extent of which is dependent on the strength of the acid used. With relatively weak acids, such as trifluoroacetic and HCl acid in acetonitrile, acidochromism in **SP** is weak with only a minor bathochromic shift upon UV-irradiation. For **NSP**, the changes are even

less apparent due to its already red-shifted absorption (due to the electron withdrawing nitro group), which rationalizes why the acidochromism of the spiro form has thus far gone essentially unnoticed. We show here that with stronger acids, protonation induced changes are clear for both **SP** and **NSP** and that both show pH-gated photochromism to the protonated merocyanine forms.

Spontaneous ring opening to the **Z-MCH⁺**/**Z-NMCH⁺** states is observed upon addition of strong acid, with subsequent reversible photo induced isomerization to the **E-MCH⁺**/**E-NMCH⁺** states. The higher acidity of the protonated **Z**-merocyanine form is demonstrated by adding an acid with a pK_a intermediate of those of **Z-MCH⁺** and **E-MCH⁺**, enabling direct photochemical switching between the **SP** and thermally stable **E-MCH⁺** form at room temperature. Understanding the acid/base switching of spiropyrans, and the requirement for matching of the pK_a of the acid with that of the merocyanine forms, allows for stable access of a total of four photochromic states and opens up a wide range of possibilities for applications as functional units. Finally, although only the spiropyran form is thermally stable at room temperature in the absence of acid and addition of acid induces spontaneous ring opening to the **Z-MCH⁺** and **E-MCH⁺** forms, by using an acid with a pK_a between that of the **Z**- and **E**-merocyanine isomers, reversible photochemical switching between thermally stable colorless **SP** and colored **E-MCH⁺** forms can be achieved at room temperature.

Experimental Section

Materials. **NSP** and chemicals used for the synthesis of **SP** were purchased from Aldrich or TCI and were used without further purification. The synthesis of **SP** is described in the supporting information, as well as characterization by NMR spectroscopy (1H , ^{13}C APT, HSQC, HMBC, COSY and NOESY) of its protonated **Z** and **E** forms generated by trifluoromethanesulfonic acid and phosphoric acid, respectively. HPLC grade acetonitrile was used for the spectroscopic studies.

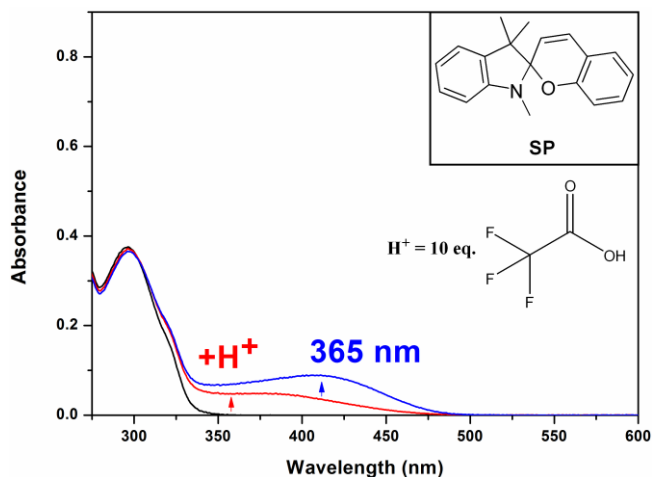
Physical Methods. NMR spectra were obtained on a Bruker 600 NMR spectrometer. Chemical shifts (δ) are reported in parts per million and coupling constants in Hertz. Integrations are reported, with multiplicities denoted as: s = singlet, d = doublet, t = triplet, br = broad singlet, m = multiplet. Chemical shifts are reported with respect to tetramethylsilane and referenced to residual solvent (CD_3HCN) signals. UV/vis absorption spectra were recorded using an Analytik Jena Specord600 spectrometer. Quantum yields were determined as described in the supporting information, with calculations concerning the protonated photochromism were performed by determining a PSS (λ_{exc} 365 nm) in the presence of strong acid of 58.9 % **E-MCH⁺** and 68.3 % **E-NMCH⁺** by scaled subtraction. The absorption spectra immediately after protonation to the **Z**-forms and both those resulting from partial deprotonation at the PSS and direct protonation of

the merocyanine forms were used for reference. Irradiation was carried out with LEDs (Thorlabs) at 365 nm (4.1 mW, M365F1), 455 nm (3200 mW, M455L3-C5), 565 nm (2.0 mW, M565F1), and 660 nm (14.5 mW, M660F1). For details of theoretical calculations see the SI.

Results and Discussion

Acidochromism of **SP** and **NSP** with weak acids.

Although the photochromism of spiropyran (**SP**) was reported earlier,²³ the photochromism of 6'-nitrospiropyran (**NSP**) is much more pronounced⁵⁵ due to resonance stabilization of the phenolate in the ring-open form (see **Scheme 1**). The merocyanine form of **NSP** is sufficiently thermally stable for photoswitching to be observed at room temperature ($\Phi = 0.03$), however, the thermal reversion of **SP** is sufficiently delayed only at -30 °C to observe photoswitching to its merocyanine form ($\Phi = 0.07$, **Figure S1**). The acidochromism of **NSP** and **SP** has been noted on several occasions, with trifluoroacetic acid in large excess,^{33-35,37,39,40} manifested in a slight bathochromic shift, that is less pronounced for **NSP** than **SP**, and in both cases results in only minor amounts of the protonated species (**Figure 1**). The limited acidochromism of **SP** and **NSP** observed with CF_3CO_2H and HCl earlier, was observed also with excess CCl_3CO_2H and, in the case of **NSP**, with H_3PO_4 (**Figure S2**) also. Irradiation at 365 nm results in a further slight bathochromic shift, which is reversed by irradiation with visible light. The greater effect on **SP** than for **NSP**, is consistent with theoretical calculations (**Table S1** in the SI).



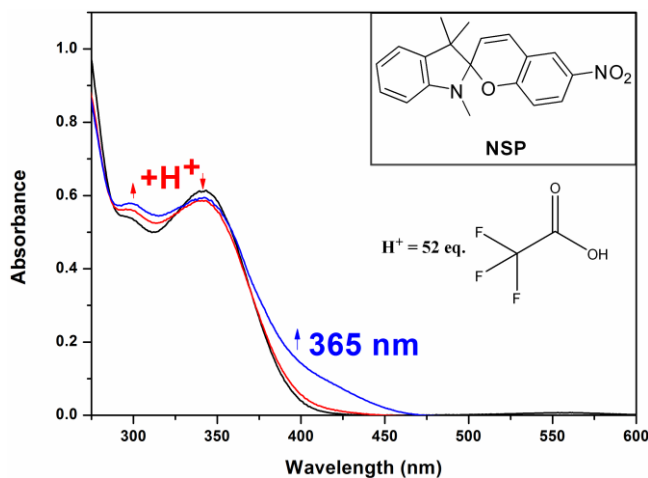


Figure 1. UV/vis absorption spectra of (top) **SP** and (bottom) **NSP** (62 μM in acetonitrile, black lines) upon addition of excess $\text{CF}_3\text{CO}_2\text{H}$ (10 and 52 equivalents, respectively, red lines) and upon subsequent irradiation at 365 nm (blue lines). Irradiation with visible light recovers the absorption spectrum prior to irradiation at 365 nm.

*pH-gated photochromism of **SP** and **NSP** with strong acids.*

In contrast to the changes observed with acids such as $\text{CF}_3\text{CO}_2\text{H}$, addition of near stoichiometric amounts of strong acids (H_2SO_4 , pK_a 8.7; $\text{CF}_3\text{SO}_3\text{H}$, pK_a 0.7; and HClO_4 , pK_a -0.7)⁵¹ to **SP** and **NSP** in acetonitrile resulted in the appearance of a well-defined absorption band assigned to Z-isomer of the protonated merocyanine form (**Figure 2** and **Figure S3**), which is unaffected by the addition of further equivalents of acid. A bathochromic shift and increase in absorptivity was induced by subsequent irradiation at 365 nm ($\Phi_{R=H} = 0.92$, $\Phi_{R=\text{NO}_2} = 0.82$) consistent with the observations of and mechanism proposed by Shiozaki and assigned as due to Z/E isomerisation.³⁸ This is also consistent with the theoretical calculations (**Table S1** in the SI) that predict a 32 nm bathochromic shift and a strong increase of the oscillator strength when going from Z-MCH⁺ to E-MCH⁺. Irradiation at 455 nm results in recovery of the Z-isomer for both **NSP** (**Figure 2**) and **SP**, even under continuous irradiation of the spectrometer (**Figure 3**), and is analogous to the behavior of spirooxazines.⁴⁷ The thermal nature of the ring-opening was confirmed by monitoring absorbance at 375 nm only (i.e. monochromatic light source) where the **SP** form does not absorb but the Z-MCH⁺ form does absorb, before and after addition of acid. The change in absorbance at 375 nm was immediate and complete with the mixing time.

The red-shift that manifests Z to E-isomerization is ascribed to the increase in electronic delocalization that accompanies increased planarity. Indeed the maximum visible absorption of the TTC isomer of the (deprotonated) merocyanine shifts from 550 nm to 595 nm in the TTT isomer (Scheme 1).^{56,57} The protonated E-merocyanines are also obtained by addition of 1 equiv. of a (strong) acid

to E-MC and E-NMC formed by irradiation of **SP** and **NSP** at -30 °C (to limit thermal reversion, **Figure S4** and **Figure 4**, respectively). Subsequent irradiation at 365 nm re-establishes the PSS obtained with acid (*vide supra*) with reversion to the Z-isomers upon irradiation at 455 nm.

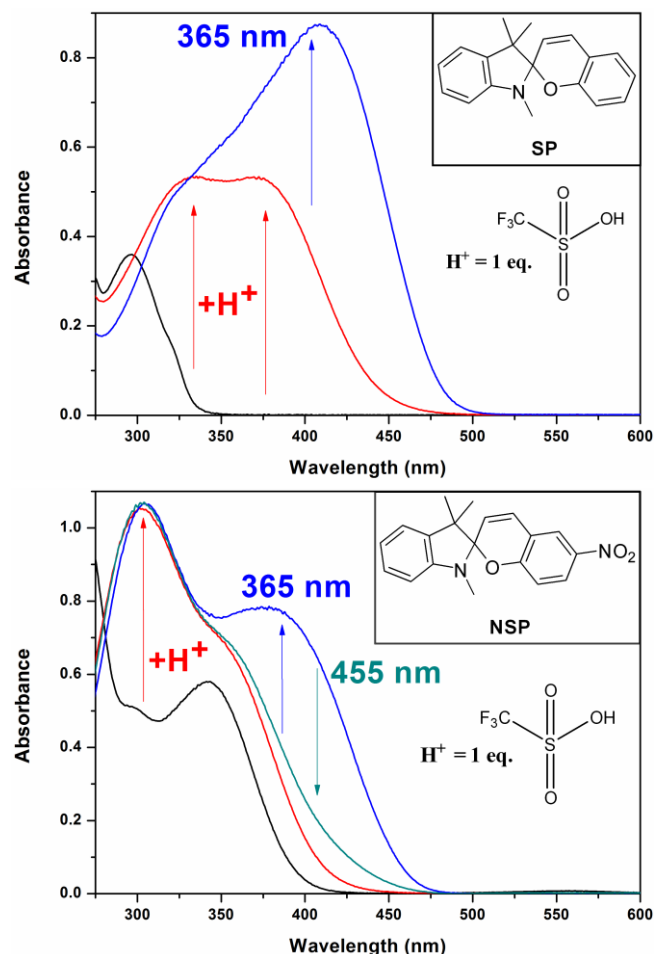


Figure 2. UV/vis absorption spectra of (top) **SP** and (bottom) **NSP** (62 μM in acetonitrile, black lines) upon addition of 1 equiv. $\text{CF}_3\text{SO}_3\text{H}$ (red lines). Irradiation at 365 nm induces a red shift to 420 nm (blue lines), which is reversed by irradiation at 455 nm (for E-MCH⁺ to Z-MCH⁺ see **Figure 3**).

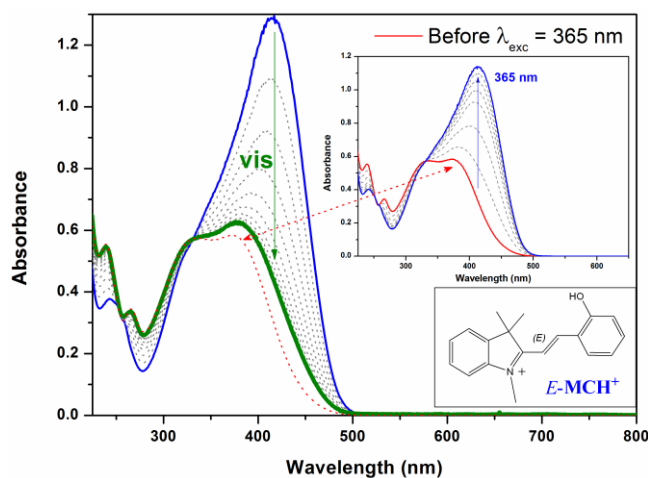


Figure 3. UV/vis absorption of the *E*-MCH⁺ form (blue line, generated by irradiation at 365 nm, inset) over time, showing near complete reversion to the initial *Z*-MCH⁺ form upon continuous visible light irradiation (by the spectrometer, spectra at 100 s intervals, while no change in absorbance was observed over 200 s in the dark).

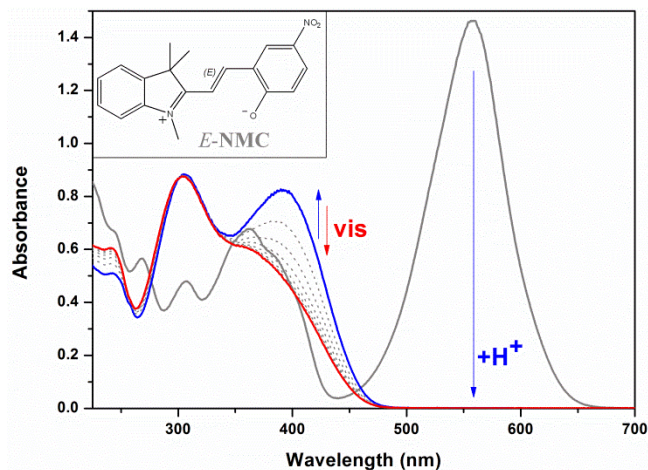
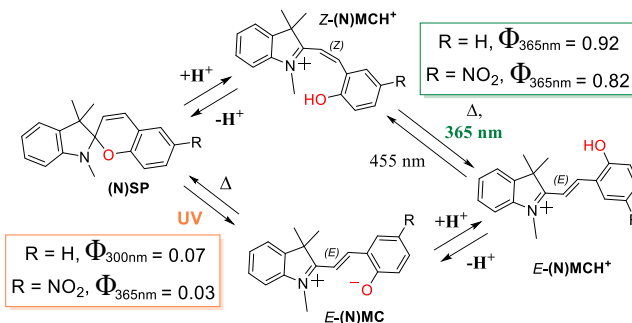


Figure 4. Low temperature UV/vis absorption spectrum of *E*-NSP and *E*-NMC generated at $-30\text{ }^{\circ}\text{C}$ by irradiation at 365 nm (grey solid line, initial concentration of NSP 52 μM). Addition of 1.5 equiv. of $\text{CF}_3\text{SO}_3\text{H}$ leads to formation of *E*-NMCH⁺ (blue solid line) with reversion to a PSS upon irradiation by the light source of the UV/Vis spectrometer (red solid line).

The acid/base dependence of the photochemistry of both spiropyrans is summarized in **Scheme 3**. The data presented here contradict earlier proposals that irradiation of the protonated *E*-merocyanine leads to the formation of the spiropyran form,^{33,34,36,58,46} based on the loss of visible absorption (i.e. decoloration). Instead it is the protonated *Z*-merocyanine that was obtained. Indeed that this is the case is apparent in the blue shifted shoulder due to the *Z*-(N)MCH⁺ form in spectra reported earlier.³⁷

Although deprotonation of MCH⁺ at the photostationary state (PSS_{365nm}) results in full recovery of the absorp-

tion spectrum of the ring closed **SP** and **NSP** forms, when base is added stepwise substoichiometrically the conversion of the *Z*-isomer is observed prior to that of the *E*-isomer (**Figure S5**). The order of recovery is consistent with the pK_a of the *Z*-isomer being less than that of the *E*-isomer, which is expected considering the contribution of ring closing to the acid/base equilibrium. Furthermore, at $-30\text{ }^{\circ}\text{C}$, a temperature at which the *E*-MC isomers are thermally stable, the visible absorption of the MC form does not appear until the sufficient base has been added to deprotonate all of the *Z*-MCH⁺ present (**Figure S6**).



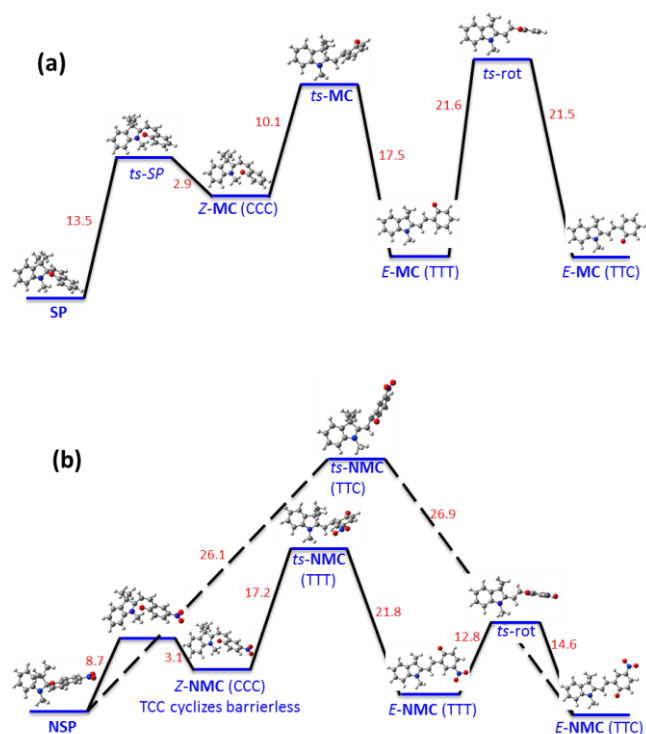
Scheme 3. pH-gated photochromism of spiropyrans and nitrospiropyrans, in absence and presence of strong acids.

Calculated energies and barriers for ring opening of *SP* and *NSP*

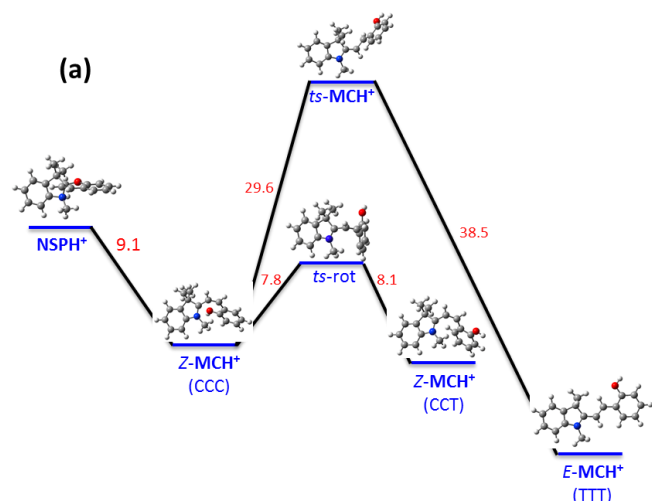
The energies of the observed isomers were calculated using a DFT known to be suited for spiropyrans, as detailed in the SI.⁴¹ The calculated energies of the unprotonated spiropyran forms relative to their merocyanine isomers are fully consistent with experimental data; i.e. that the ring-open form is thermally accessible from the **NSP** form. Interestingly, a comparison between the computed Raman spectra with those measured experimentally for the non-protonated **SP** and **NSP** forms (**Figure S7** and **Figure S10**), as well as for the protonated *Z*-MCH⁺ and *E*-MCH⁺ show a good qualitative match, which supports that the selected level of theory is well suited for our purposes.

The lowest energy **MC** form, the TTT, lies 3.2 kcal/mol higher than the ring-closed **SP** form and has a 17.5 kcal/mol barrier from the *E* to *Z* form before undergoing low-barrier ring-closing. The lowest energy **NMC** form, on the other hand, is the TTC conformer, which is 0.8 kcal/mol lower in energy than the ring-closed form, though closely followed by the TTT (1.8 kcal/mol). Furthermore, the TTC form, which is the main species observed experimentally also for nitrospiropyrans^{32,59–61} (with in acetonitrile one order of magnitude greater abundance than the TTT form)⁶², has a significantly higher barrier to conversion to the *Z*-NMC form (26.9 kcal/mol for direct conversion, 21.8 kcal/mol for conversion through the TTT form). These data are consistent with its observed thermal stability at room temperature. Notably, theory shows that even if the indolinic nitrogen is protonated, as pro-

posed earlier,^{33,36} proton transfer coupled with C_{spiro}-O bond cleavage is barrierless and yields the thermally more stable Z-merocyanine form (**Scheme 5**).



Scheme 4. Computed free energy profiles for the optimized lowest energy conformers of (a) **SP** and (b) **NSP** in the ring-closed spiropyran and ring-open merocyanine forms, and the barriers to their interconversion. All energy differences given in kcal/mol.



Scheme 5. Computed free energy profiles for the optimized lowest energy conformers of the protonated forms of (a) **SP** and (b) **NSP**. See caption of Scheme 3.

The barriers are significantly higher than those of the unprotonated forms, ranging from 29.6 (**Scheme 5a**) to 39.4 (**Scheme 5b**) kcal/mol, consistent with their experimentally observed thermal stability. The photochemical interconversion between the Z- and E-merocyanine forms thus enables controlled access over two distinct protonated states as shown, through the energetic entrapment of the respective isomers.

Re-enabling room temperature switching of **SP**

The difference in the pK_a s of the Z and E-merocyanine isomers additionally opens the possibility to gate the photochromism of **SP** with pH. In large excess, H_3PO_4 induces formation of Z-MCH⁺ (**Figure S7**), whereas near stoichiometric amounts have essentially no effect on the absorption spectrum of **SP**. Remarkably, in presence of equimolar phosphoric acid at room temperature solely the E-MCH⁺ isomer is generated both upon irradiation at 300 nm (**Figure 5**) and thermally over time (**Figure S8**), with full recovery to the unprotonated **SP**-form upon subsequent irradiation at 455 nm. This effect is observed because the pK_a of H_3PO_4 lies between that of the E- and Z-MCH⁺ isomers. Any $H_2PO_4^-$ present will deprotonate Z-MCH⁺ spontaneously inducing ring closing, while any photogenerated E-MC will undergo protonation by H_3PO_4 preventing thermal reversion and thus enables essentially direct photoconversion between **SP** and E-MCH⁺ forms through the Le Chatelier principle (**Scheme 6**) despite that **SP**/E-MC photochromism is thermally inhibited at room temperature. Furthermore, the thermal stability of the E-MCH⁺ formed in the presence of near-stoichiometric amounts of H_3PO_4 allows for its characterization by NMR spectroscopy (1H , ^{13}C APT, HSQC, HMBC, COSY and NOESY), as well as that of the Z-MCH⁺ form generated by addition of CF_3SO_3H (see the SI).

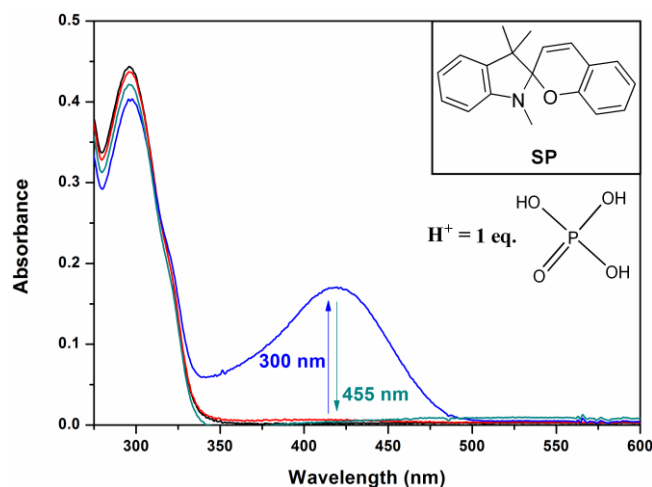
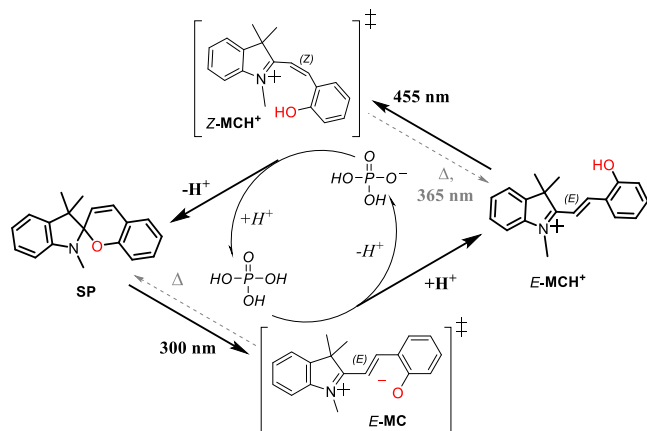


Figure 5. UV/vis absorption spectra of **SP** (62 μM in acetonitrile, black line) with 1 equiv. H_3PO_4 (red line) followed by Irradiation at 300 nm (to form **E-MCH⁺**, blue line), while irradiation at 455 nm recovers the **SP** form.



Scheme 6. Unidirectional cyclic interconversion between **SP** and **E-MCH⁺** upon pH-gated photochromism in near stoichiometric presence of H_3PO_4 .

Conclusions

In conclusion, we show through a combined experimental and theoretical study that the acidochromism of spiropyrans is highly dependent on the strength of the acid used in aprotic solvents, with acids, such as $\text{CF}_3\text{CO}_2\text{H}$ and HCl , used typically, being too weak to protonate the **Z-(N)MC** isomer. Fully pH-gated photochromism of simple spiropyrans is achieved with stronger acids (e.g., $\text{CF}_3\text{SO}_3\text{H}$), manifested in the two-state photoisomerization of **Z-(N)MCH⁺**/**E-(N)MCH⁺** and, together with **(N)SP**/**E-(N)MC** photoisomerization, leads to an overall four-state molecular switching cycle. In retrospect, the reactivity reported in the present study implies that in earlier studies the **Z-(N)MCH⁺** form may have been observed erroneously assigned as the expected ring-closed spiropyran form. The theoretically computed energies agree with the experimentally observed forms and, moreover, underline the increased stability of the **Z-** and **E-**

isomers through significantly higher thermal barriers than in the deprotonated states. Additionally, in contrast to conclusions drawn earlier regarding the protonation of spiropyrans,^{33,34,36,37,45,46,48} theory suggests that the protonation of the indolinic nitrogen leads to barrierless proton transfer to the phenolate. Hence, even if an acid is strong enough to protonate the indolinic nitrogen, spontaneous ring-opening to the **Z-(N)MCH⁺** form would make such a protonation transient at most. Finally, by selecting an acid such that its pK_a lies between that of the **Z-** and **E-MCH⁺** isomers (e.g., H_3PO_4 in the case of **SP**), enables gated photochromism and a unidirectional multi-state interconversion between spiropyran and merocyanine species at room temperature. The nitro group of **NSP** is electron withdrawing in comparison with **SP** and, as such, stabilizes the merocyanine form both in the deprotonated form and as a leaving group in the ring opening process. As a counter poise to these effects, however, the nitro group decreases the pK_a and hence the strength of acid required to achieve thermal ring opening needs therefore to be greater. Overall, however, the nitro-group of **NSP** does not appear to affect the mechanisms involved in comparison with **SP**.

The pK_a dependent control of the state of the photochrome opens new opportunities in the application of spiropyrans in photocontrol of pH and in understanding the influence local pH changes (e.g., at surfaces of electrodes) have on spiropyran based electrochemical devices.

ASSOCIATED CONTENT

Details of synthesis and characterization of **SP**, with NMR spectroscopic characterization (^1H , ^{13}C APT, HSQC, HMBC, COSY and NOESY) of both **Z-MCH⁺** and **E-MCH⁺**, actinometry, computational studies, experimental and calculated Raman spectra of the **SP/NSP** forms and **Z-MCH⁺**/**Z-NMCH⁺** and **E-MCH⁺**/**E-NMCH⁺** forms, and additional UV/vis absorption spectral data can be found in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ABBREVIATIONS

SP, 1,3,3-trimethylbenzoindolinopyrrolospiroopyran; NSP, 6'-nitro-1,3,3-trimethylbenzoindolinopyrrolospiroopyran; MC, 1,3,3-trimethylbenzoindolinopyrrolomerocyanine; NMC; 6'-nitro-1,3,3-trimethylbenzoindolinopyrrolomerocyanine.

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