Blockade of persistent colored isomer formation in photochromic 3H-naphthopyrans by excited-state intramolecular proton transfer

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In photochemistry the excited-state intramolecular proton transfer process (ESIPT) is often observed as a highly efficient singlet excited state depletion pathway, which in the presence of a strong intramolecular hydrogen bond may proceed on a subpicosecond time scale. The present work describes the suppression of unwanted transoid-trans isomer formation in photochromic 3H-naphthopyran derivatives by the introduction of a 5-hydroxy substituent. According to time-resolved spectroscopy experiments and excited-state ab initio calculations, transoid-cis → transoid-trans photoisomerization is reduced by a competitive ESIPT channel in nonpolar solvent (cyclohexane). Upon specific solute–solvent interactions (methanol, acetonitrile) the intramolecular hydrogen bond in the transoid-cis form is perturbed, favoring the internal conversion \( S_1 \rightarrow S_0 \) process as photostabilizing channel.

The proton transfer (PT) reaction is known to play an important role in a variety of biological and physical processes. A proton may be transferred in either the ground or the excited electronic state along the intramolecular hydrogen bond of the molecule, or along the intermolecular hydrogen bond in its complexes. PT plays many important functions in nature, e.g. the excited-state intramolecular proton transfer (ESIPT) process is known to be responsible for photostability of DNA bases due to the presence of multiple intermolecular hydrogen bonds linking the base pairs. Moreover, the ESIPT process is a common reaction in many internally H-bonded organic molecules and thus may play an essential role in many applications, e.g., in organic photostabilizers—the compounds used for protection of synthetic polymers against degradation caused by UV components of sunlight. ESIPT can also lead to photochromic functionality, e.g. in Schiff bases. The ESIPT phenomenon was utilized as a photoswitching mechanism in internally hydrogen-bonded molecules. The search for proton cranes, in which a proton can be transferred over long distances through large-amplitude motion, is still a hot topic.

The ESIPT process specifically between a hydroxyl group and an adjacent carbonyl group has been observed to proceed with a small energy barrier in quite a few chemical families. For example, rapid ESIPT has been implicated as a key factor in the photostability of naturally occurring hydroxyanthraquinone red colorants found in art masterpieces and illuminated manuscripts. Ab initio studies on 5,6-dihydroxyindole (in which the 5-hydroxyl tautomerizes to a carbonyl) suggest a barrierless ESIPT as the key energy shunt pathway responsible for the photoprotective properties of eumelanin. A similar process occurs in hydroxychromones, hydroxyflavones, and hydroxyquinolones. Furthermore, ESIPT can either be coupled to, or compete with other processes. For example, 3-hydroxypicolinic acid engages in a double ESIPT and a designed quinoxalinylsalicylaldehyde can undergo either a normal ESIPT to the adjacent carbonyl, or an excited state long-range proton transfer (ESLRPT) to the more distant quinolinyl nitrogen, depending upon the excitation wavelength.

Importantly, the photophysics and photochemistry of molecular systems (especially their \( S_1 \)-state energetic landscape) can be tuned by chemical modifications that may activate the ESIPT pathway, which upon strong intramolecular hydrogen bonding may proceed on subpicosecond time scale and with high efficiency at the expense of other competitive reaction channels in the excited state. For instance, such a strategy can be used to...
reduce triplet excited state formation in order to minimize side-effects in UV sunscreens (2-hydroxybenzophene-based derivatives)\(^3\). Similarly, the present work leverages ESIPT to suppress the unwanted photochemical channel of transoid-cis $\rightarrow$ transoid-trans photoisomerization in 3\(H\)-naphthopyrans (NP). For this purpose, we chose 5-hydroxy-NP (5-(OH)-NP) as a model compound (Fig. 1).

3\(H\)-Naphthopyrans constitute a unique family of compounds that not only have advantageous photochromic properties for use in commercially available photochromic lenses, but also can be easily synthetically modified to obtain desired spectroscopic and photophysical properties\(^3\)–\(^8\). The UV-induced coloration in NP compounds occurs via a barrierless photodissociative ring opening of the colorless pyranoid closed form (CF), leading to the formation of a colored open-form transoid-cis (TC) isomer\(^3\)\(^9\). During this process, or upon TC photoexcitation, a transoid-trans (TT) side product is produced if the excited-state energy landscape favours a single-twist rotation along the C\(_{14}\)=C\(_1\) axis\(^4\)\(^0\),\(^4\)\(^1\). However, the presence of TT in photochromic systems may be unwanted in some applications, such as photochromic lenses, due to the substantially longer TT vs. TC lifetime (hours vs seconds), which leads to prolonged fading rates after the cessation of UV exposure\(^4\)\(^2\),\(^4\)\(^3\). The thermal fading TT $\rightarrow$ TC is hampered by a high energy barrier (ca. 1.3 eV\(^3\)\(^9\)).

In this study we demonstrate with the 5-hydroxy-NP model compound that TT formation can be suppressed by the intervention of ESIPT. This principle may be important for the development of ESIPT-based NP derivatives for photochromic materials with reduced TT contribution.

### Experimental

**Materials.** 3,3-Diphenyl-5-hydroxy-3\(H\)-benzo[\(f\)]chromene (5-(OH)-NP) was synthesized following the procedures described in the Supplementary Information. In the time-resolved spectroscopic investigations cyclohexane, methanol and acetonitrile of spectroscopic grade from Sigma Aldrich were used for solution preparation. Studies were performed vs. a reference compound 3,3-diphenyl-3\(H\)-naphtho[2,1-\(b\)]pyran (5-(H)-NP) purchased from TCI.

**Time-resolved UV–Vis spectroscopy.** Changes in UV–Vis absorption spectra and kinetics on a time scale of seconds were recorded for solutions in a 1 cm x 1 cm fused silica cuvette. Conditions of 21 °C were achieved by placing the sample into a temperature-controlled cuvette holder (Flash 300, Quantum Northwest) with stirring switched on. UV LED (\(\lambda_{exc} = 340\) nm, Thorlabs M340L4) was used to induce the photochromic reaction. UV–Vis probing light was generated by a xenon lamp (Applied Photophysics), equipped with a bundle fiber. The probing beam was passed through a long-pass filter (WG 280) and an almost-closed iris to ensure low light intensity in the cell. The UV–Vis spectra were recorded by an Ocean Optics FLAME-T-VIS-NIR-ES USB spectrometer at the sampling rate of 20 spectra per second.

Femtosecond UV–Vis transient absorption spectra were obtained using a commercially available system (Ultrafast Systems, Helios)\(^4\)\(^5\). The ultrafast laser system consists of a short-pulse titanium-sapphire oscillator (Mai-Tai, Spectra Physics, 70 fs) followed by a high-energy titanium-sapphire regenerative amplifier (Spitfire Ace, Spectra Physics, 100 fs). The 800 nm beam was split into two beams to generate: (1) a pump (\(\lambda_{exc} = 444\) nm)
in the optical parametric amplifier (Topas Prime with a NirUVVis frequency mixer) and (2) probe pulses—white light continuum in the UV–Vis (330–660 nm) range by using CaF$_2$ plate. The remaining 800 nm photons in the probe pulse were filtered out before the sample: 5-(OH)-NP solution in a quartz cell 2 mm thick with stirring. Photostationary state of TC population was obtained by the continuous UV LED irradiation at 340 nm. For selective excitation of the population, the excitation wavelength was set at $\lambda_{\text{exc}} = 444$ nm with a pump pulse energy of 1 $\mu$J. The transient absorption data were corrected for chrip of white light continuum.

The obtained transient absorption spectra were analyzed using the global fitting procedure (ASUFIT program) and satisfactory fits were obtained with single- or double-exponential fits. Convolution with the instrument response function (200 fs, FWHM) was included in the fitting procedure. The accuracies of the obtained time-constants derived from analysis of transient absorption results were as follows: 5% (UV–Vis data in time window over tens/hundreds of seconds) and 10% (ultrafast UV–Vis data).

**Computational details.** The equilibrium geometries of the 5-(OH)-NP isomers in their closed-shell ground state ($S_0$) were obtained with the MP2 method without imposing any symmetry constraints. The energy of the most stable form CF$_1$ is the reference energy for higher energy structures. The excited-state ($S_1$) equilibrium geometries were determined with the second-order algebraic diagrammatic construction ADC(2) method. The correlation-consistent valence double zeta basis set with polarization functions on all atoms (cc-pVDZ) was used in these calculations, as well as in potential energy profiles and surfaces. The vertical excitation energies and response properties of the lowest excited singlet states were calculated using the CC2 methods. The basis set augmented with the diffuse functions aug-cc-pVDZ was also used to compute vertical excitation energies of the molecular system. All calculations were performed using the TURBOMOLE program package.

**Results and discussion**

**Ground state energy landscape and vertical excitation energies of 5-(OH)-NP.** The studied 5-hydroxy 3H-naphthopyran (5-(OH)-NP) possesses two closed-conformer CNH minima in the ground electronic state ($S_0$). The most stable is the CF$_1$ form, which is stabilized by the O$_3$–H–O$_2$ hydrogen-bond between the two neighboring oxygen atoms (Table 1). The second CF$_2$ minimum, with the hydroxyl group rotated about 180°, is 0.156 eV higher in energy. As shown in Table 1, the $S_0$ → $S_1$ absorption maximum (strongest absorption) of the H-bonded CF$_1$ form is bathochromic by 0.12 eV vs. the rotated CF$_2$ form. Photoexcitation of the colorless CF form (CF$_1$ or CF$_2$) leads to the respective colored isomers (TC$_1$ or TC$_2$, respectively) in a barrierless process in the $S_1$ excited state, the behaviour of which is similar to the previously studied unsubstituted parent NP molecule. The photogenerated TC$_1$ conformer is also stabilized by an intramolecular hydrogen bond vs. the rotated TC$_2$ compartment, (0.407 eV vs. 0.752 eV). Such a large stabilization energy causes the TC$_2$ form to predominate over the TC$_2$ population under typical experimental conditions.

The calculated $S_0$-state energy barrier for free rotation of the hydroxyl group (TC$_1$ → TC$_2$) is +0.17 eV or +0.18 eV, depending on the rotation side (MP2/cc-pVDZ). Again, similar to CF, the absorption maximum of H-bonded TC$_1$ is slightly red-shifted vs. the rotated TC$_2$ isomer (see Table 1). Stabilization of TC$_1$ by intramolecular hydrogen bonding explains why for freshly prepared solutions of 5-(OH)-NP a small amount of TC species is observed by a weak absorption band with maximum at 443 nm (Fig. S1). Its content is roughly estimated at 0.8% in cyclohexane, and a similar amount of 1.0–1.5% was estimated in CDCl$_3$ by 1H-NMR spectra integration (see Supplementary Information). Interestingly, the band absorption is less pronounced in methanol and acetonitrile (Fig. S1), likely due to disruption of the internal hydrogen bond in TC by solute–solvent specific interactions. Such an equilibrium between TC and CF has been reported for a similar NP derivative.

To explore this phenomenon, various TC and methanol (1:1) complexes were calculated (Fig. S2A). The most stable complex is MC1 with one hydrogen bond formed between the O$_3$ hydroxyl group and the methanol acting as a proton acceptor, and a second H-bond formed between the O$_2$ oxygen atom and the methanol acting as a proton donor. Such double hydrogen bond formation stabilizes the TC–methanol complex. However, the intramolecular hydrogen bond is weakened (length is 2.373 Å). In the case of complexes with acetonitrile (Fig. S2B), interactions are related to ππ stacking interactions and hydrogen bonding.

**Thermally activated fading process of the TC isomer to colorless CF.** The TC isomer plays a key role as a coloured species in the photochromic reaction of NP derivatives. TC decay occurs in a two-step reaction leading to CF via a high-in-energy cisoid-cis intermediate INT form. The timescale of the TC form depopulation depends strongly on the ratio of the $S_0$ state energy barriers, $\Delta E$, separating this cisoid-cis intermediate from the neighboring stable conformers: colored TC (\$\Delta E^{\text{INT-TC}}\$) and colorless CF (\$\Delta E^{\text{INT-CF}}\$), see Fig. 241,53.

The $\Delta E$ relative energy of 0.407 eV for 5-(OH)-NP is much lower than that for the 5-(H)-NP derivative (0.588 eV)\textsuperscript{19}, mainly due to the internal hydrogen bond in the TC$_1$ form of 5-(OH)-NP. Conversely, the larger relative energy of TC$_2$ (0.752 eV) is due to O$_3$–O$_2$ repulsion, which is absent in 5-(H)-NP. The relative energy of the rotated TC$_2$ isomer is higher (0.752 eV) than that of TC$_1$ (0.407 eV); consequently, in inert solution such as cyclohexane the equilibrium is shifted towards TC$_1$.

The TC isomers constitute relatively deep minima on the $S_0$ state potential-energy profile, separated from the INT intermediate by the $\Delta E^{\text{INT-to-TC}}$ energy barrier of +0.466 eV in the case of H-bonded TC$_1$ (Table 2), which is slightly larger than for 5-(H)NP (+0.452 eV)\textsuperscript{30}. Despite the large barrier, the process leading to CF is thermally available due to its exothermic character. However, the high-in-energy intermediate INT must first be populated. Once INT is formed, it turns out that the energy barrier (\$\Delta E^{\text{INT-CF}}\$) for the forward process (\$\text{INT}_1 \rightarrow \text{CF}_1\$) is much larger (+0.313 eV) than the corresponding barrier (\$\Delta E^{\text{INT-TC1}}\$) toward TC$_1$ (+0.235 eV).
| $S_0$ form | $\Delta E^{zz}$ | $\lambda_{abs}$ | $f$ | $\mu_z$ |
|-----------|----------------|----------------|-----|--------|
| Colorless CF forms |
| 5-(OH)-CF (H-bonded), CF$_1$ | $S_0$ | 0.00 | $\mu_z = 2.3$ | |
| $S_0 \rightarrow S_1(\pi\pi^*)$ | 3.81 | 0.035 | 1.00 | |
| $S_0 \rightarrow S_2(\pi\pi^*)$ | 3.88 | $\textbf{0.208}$ | 2.74 | |
| $S_0 \rightarrow S_3(n\pi^*)$ | 4.71 | 0.009 | 2.32 | |
| $S_0 \rightarrow S_4(n\pi^*)$ | 4.75 | 0.058 | 3.35 | |
| 5-(OH)-CF (rotated), CF$_2$ | $S_0$ | 0.156$^*$ | $\mu_z = 1.1$ | |
| $S_0 \rightarrow S_1(\pi\pi^*)$ | 3.81 | 0.036 | 1.55 | |
| $S_0 \rightarrow S_2(\pi\pi^*)$ | 4.00 | $\textbf{310}$ | $\textbf{0.176}$ | 3.87 |
| $S_0 \rightarrow S_3(n\pi^*)$ | 4.69 | 0.000 | 3.44 | |
| $S_0 \rightarrow S_4(n\pi^*)$ | 4.81 | 0.003 | 8.26 | |
| Colored TC forms |
| 5-(OH)-TC (H-bonded), TC$_1$ | $S_0$ | 0.407$^a$ | $\mu_z = 3.8$ | |
| $S_0 \rightarrow S_1(\pi\pi^*)$ | 2.55 | $\textbf{486}$ | 0.075 | 6.75 |
| $S_0 \rightarrow S_2(\pi\pi^*)$ | 2.96 | $\textbf{420}$ | $\textbf{0.771}$ | 6.27 |
| $S_0 \rightarrow S_3(\pi\pi^*)$ | 3.14 | 0.016 | 0.79 | |
| $S_0 \rightarrow S_4(\pi\pi^*)$ | 4.01 | 0.093 | 5.77 | |
| 5-(OH)-TC (rotated), TC$_2$ | $S_0$ | 0.752$^a$ | $\mu_z = 2.5$ | |
| $S_0 \rightarrow S_1(\pi\pi^*)$ | 2.73 | $\textbf{453}$ | 0.175 | 4.15 |
| $S_0 \rightarrow S_2(\pi\pi^*)$ | 2.87 | $\textbf{432}$ | 0.186 | 3.12 |
| $S_0 \rightarrow S_3(\pi\pi^*)$ | 3.13 | $\textbf{396}$ | $\textbf{0.509}$ | 4.63 |
| $S_0 \rightarrow S_4(\pi\pi^*)$ | 4.09 | 0.105 | 4.52 | |
| $S_0 \rightarrow S_5(n\pi^*)$ | 4.32 | 0.004 | 9.09 | |
| $S_0 \rightarrow S_6(\pi\pi^*)$ | 4.40 | 0.205 | 3.17 | |

Colored TT forms

Continued
Thus, one can expect recovery of the TC$_1$ isomer as the most probable path (Fig. 2), which suggests a rationale for the long apparent TC$_1$ lifetime in solution for 5-(OH)-NP vs. 5-(H)-NP.

Table 1. Vertical excitation energy, $\Delta E^{\text{VE}}$ (in eV) and $\lambda_{\text{abs}}$ (in nm), oscillator strength, $f$, and dipole moment, $\mu_e$ (in Debye), of the lowest excited singlet states calculated with the CC2/aug-cc-pVDZ method for the 5-(OH)-NP ground state equilibrium forms optimized at the MP2/cc-pVDZ theory level. Dipole moment of the ground-state, $\mu_g$ (in Debye, MP2/cc-pVDZ). $^a$Difference in adiabatic energy ($E^a$, in eV) relative to the closed form, CF$_1$, calculated at the MP2/cc-pVDZ theory level. Significant values are in [bold].

| $S_0$ form                              | $\Delta E^{\text{VE}}$ | $\lambda_{\text{abs}}$ | $f$  | $\mu_e$ |
|----------------------------------------|------------------------|-------------------------|------|---------|
| 5-(OH)-TT (H-bonded), TT$_1$           |                        |                         |      |         |
| $S_0 \rightarrow S_1(\pi\pi^*)$       | 0.438$^a$              |                         | 3.7  |         |
| $S_0 \rightarrow S_2(\pi\pi^*)$       | 2.68                   | 463                     | 0.122| 5.82    |
| $S_0 \rightarrow S_3(\pi\pi^*)$       | 3.06                   | 405                     | 0.670| 7.42    |
| $S_0 \rightarrow S_4(\pi\pi^*)$       | 3.33                   |                         | 0.023| 1.08    |
| $S_0 \rightarrow S_5(\pi\pi^*)$       | 4.11                   |                         | 0.062| 5.72    |
| $S_0 \rightarrow S_6(\pi\pi^*)$       | 4.37                   |                         | 0.216| 2.89    |
| $S_0 \rightarrow S_7(\pi\pi^*)$       | 4.39                   |                         | 0.022| 11.96   |
| 5-(OH)-TT (rotated), TT$_2$            |                        |                         |      |         |
| $S_0 \rightarrow S_1(\pi\pi^*)$       | 0.760$^a$              |                         | 2.8  |         |
| $S_0 \rightarrow S_2(\pi\pi^*)$       | 2.82                   | 440                     | 0.206| 3.92    |
| $S_0 \rightarrow S_3(\pi\pi^*)$       | 3.11                   | 399                     | 0.308| 1.40    |
| $S_0 \rightarrow S_4(\pi\pi^*)$       | 3.25                   | 381                     | 0.284| 5.48    |
| $S_0 \rightarrow S_5(\pi\pi^*)$       | 4.20                   |                         | 0.074| 4.55    |
| $S_0 \rightarrow S_6(\pi\pi^*)$       | 4.37                   |                         | 0.178| 4.88    |
| $S_0 \rightarrow S_7(\pi\pi^*)$       | 4.46                   |                         | 0.028| 8.22    |

Figure 2. Thermal decoloration of TC $\rightarrow$ CF for 5-(OH)-NP compound (black line) involves two reaction steps TC $\rightarrow$ INT and INT $\rightarrow$ CF (the first step is reversible). $S_0$-state potential-energy profiles were computed with aid of the MP2/cc-pVDZ method. The reference compound 5-(H)-NP (blue curve) is traced according to reported data.$^{53}$

Thus, one can expect recovery of the TC$_1$ isomer as the most probable path (Fig. 2), which suggests a rationale for the long apparent TC$_1$ lifetime in solution for 5-(OH)-NP vs. 5-(H)-NP.

Apparent TC fading rate and lack of TT population in changes of UV–Vis absorption spectra. In our previous studies of NP photochromic reactions, LED light at $\lambda = 365$ nm was used for
estimate a similar quantum yield for the parent compound in acetonitrile.\(^{54}\)

5-(H)-NP

calculated dipole moment for TC may facilitate conical intersection CI (S\(_{1}/S\)_0) leading to the S\(_0\) state with a less advanced change in the twist angle in cyclohexane for 60 s produces a photostationary state (PSS, Fig. 3A).

NP (see Fig. S1), LED light at \(\lambda = 340\) nm was selected for this investigation. UV irradiation of 5-(H)-NP are from reference.\(^{53}\) 5-(H)-NP theory level. Results for TC photoexcitation.\(^{39–41}\) However, since the absorption for after ceasing UV irradiation at the moment \(t = 0\) s. The initial absorption spectrum 5-(OH)-NP shows a positive bleach. Subsequently, the decay of the TC decay of the TC in contrast to 5-(H)-NP (Fig. 3D), which shows the presence of the TT formation is disfavored. This trend, although less pronounced, has been already observed for 5-(OH)-NP (see Fig. S3). The reduced yield of the photoisomerization path TT insertion of the hydroxyl group at position 5 suppresses the TC formation channel. A substantial TT lifetime elongation effect was predicted by theoretical calculations (section above). Upon decay of the TC absorption band, a practically baseline level is reached after a few hundreds of seconds (Fig. 3C), so one can insertion of the hydroxyl group at position 5 suppresses the TT formation channel. A substantial TT reduction is clearly observed (compare Fig. 3C vs. 3D), and only a very low concentration of TT can be detected for 5-(OH)-NP (see Fig. S3). The reduced yield of the photoisomerization path TC -> TT could be explained by a strong competitive channel, which is probably ESIPT in cyclohexane. As we mentioned above, the intramolecular hydrogen bond in TC (from 5-(OH)-NP) is likely disrupted in methanol or acetonitrile solution, so the ESIPT process is less probable in these solvents. Nevertheless, reduced TT formation is observed (see Figs. S4 and S5). The photostabilization of the TC species in these solvents is probably mediated by solvent polarity—note that calculated dipole moment for TC in the S\(_1\) state is high (Table 1). Stabilization of TC in the S\(_1\) state in polar solvent may facilitate conical intersection CI (S\(_{1}/S\)_0) leading to the S\(_0\) state with a less advanced change in the twist angle C\(_{14}\)←C\(_{2}\), thus TT formation is disfavored. This trend, although less pronounced, has been already observed for the parent compound 5-(H)-NP in acetonitrile.\(^{41}\)

According to Table 3, the apparent S\(_0\) ground state TC lifetime is longer for 5-(OH)-NP vs. 5-(H)-NP. The largest difference is observed in cyclohexane (factor of 7) due to the presence of the intramolecular hydrogen bond for 5-(OH)-NP stabilizing the TC form. The presumed breaking of the intramolecular H-bond in

Table 2. Energetics of the two-step process of the TC form depopulation (TC ↔ INT → CF) for 5-(OH)-NP vs. 5-(H)-NP. Adiabatic S\(_{1}\) state energies, \(E^0\), in eV, and dipole moment, \(\mu_{D}\), in Debye, for the relevant minima: TC, INT, CF, and transition states separating these minima: TS\(_1\) and TS\(_2\), calculated at the MP2/cc-pVDZ theory level. Results for 5-(H)-NP are from reference.\(^{35}\)
Figure 3. (A) Changes in absorption at probe 443 nm caused by UV irradiation ($\lambda = 340$ nm, 4 mW/cm$^2$) of 5-(OH)-NP in cyclohexane at 21 °C. (B) The initial rise in absorption upon switching on UV irradiation for two solutions 5-(OH)-NP and 5-(H)-NP in cyclohexane prepared with the same absorption ($A(340$ nm, 1 cm) = 0.32). (C, D) Evolution of $\Delta A$ spectra after ceasing UV irradiation at $t = 0$ s for 5-(OH)-NP and 5-(H)-NP, respectively.

Table 3. Photophysical properties of TC in solution: $S_0$ absorption band maximum and lifetime $\tau_{S0}$ with 5% accuracy (at 21 °C).
polar solvents such as methanol and acetonitrile has been also postulated for structurally related 3-hydroxychr-

omone 26, 55. Even if a weakened intramolecular hydrogen bond in TC is present in methanol (Fig. S2), calcula-
tions performed for MC1 complex show a decrease in the ΔEINT-CF barrier and an increase in ΔEINT-TC barrier in comparison to the isolated 5-(OH)-NP (H-bonded) molecule (see Table 2). Thus, the shortening of the S0 TC lifetime in methanol in relation to cyclohexane can be rationalized.

Properties of the excited TC isomer. For most NP derivatives photoexcitation of the TC isomer to its Franck–Condon region results in an excited S1-state geometrical relaxation, in which rotations about the two double bonds C14=C1 and C2=C3 are activated 40, 41. But in 5-(OH)-TC the S1 state relaxation is additionally accompanied by the barrierless excited-state intramolecular proton transfer (ESIPT) from O5 to O4 to produce a proton-transferred species. The minimum energy of the TC*-proton transferred species of 5-(OH)-NP was found to be lower in energy (Ea = 1.305 eV) vs. the corresponding TC* species from 5-(H)-NP (Ea = 1.948 eV) 40, due to presence of the stabilizing intramolecular hydrogen bond O5···H-O4 (see Fig. 4). Another observation is that the relaxed S1 TC minimum occurs with an optimized θ1 (C14=C1) dihedral angle of ~ 39° (see left square in Fig. 4), much lower than 90°, where the S0-state energy barrier is seen (right square in Fig. 4). Thus, upon S1 → S0 internal conversion, a species in the S0 state is produced with geometry which, in the next step, follows the S0-state gradient toward the S0 TC global minimum. This barrierless process confirmed by geometry optimiza-
tion is accompanied by the back proton transfer from O4 to the O5 oxygen atom (i.e. ground state intramolecular proton transfer, GSIPT). Note that alternative pathways, such as TC → TT isomerization, are suppressed due to a S0-state high-energy wall (Fig. 4). Moreover, note that the θ1 (C14=C1) dihedral angle of 39° found for the TC
Confirmation of ESIPT by ultrafast transient absorption studies. To confirm the ESIPT process predicted by theory in the gas phase, for experimental work the inert solvent cyclohexane was selected. Thus, for ultrafast studies, a solution of 5-(OH)-NP in cyclohexane was prepared and the sample was continuously irradiated by LED at 340 nm to generate a photostationary state (PSS). As described above, in PSS practically the only ultrashort timescales, a solution of 5-(OH)-NP in cyclohexane was continuously irradiated by LED at 340 nm to generate a photostationary state (PSS). As described above, in PSS practically the only colored form is TC. In the pump-probe experiment, a laser-pulse excitation wavelength of 444 nm was chosen for selective TC photoexcitation. Figure 5A shows UV–Vis transient absorption recorded in the time window from 0.2 to 100 ps.

At the initial delay of 0.2 ps the positive bands at 360 and 520 nm are clearly observed. Two assignments for these bands can be considered. One is that the initial positive spectrum belongs to the population product—TC*→proton transferred, since the transfer of the proton can be faster than our temporal resolution (< 200 fs), in agreement with theoretical calculations (barrierless process) and the ultrafast character of such processes in analogous molecular systems (3-hydroxyflavone27). But such an assignment does not agree with the calculated electronic transition S1→S0 for TC*→proton transferred (see Table S2). The alternative assignment for the initial positive band is TC*. Indeed, the spectral shape is reminiscent of the recorded data for TC* from 5-(H)-NP54. Thus, the positive bands at 360 and 520 nm correspond to S1→S0 and S1→S0 transitions of TC* population (n > m), while the negative band peaking at about 440 nm can be attributed to TC bleaching. On the basis of global analysis (Fig. 5B), the TC excited-state lifetime is only 0.2 ps vs. 0.8 ps (5-(OH)-NP vs. 5-(H)-NP). This shortened TC lifetime effect can be explained by ESIPT, which drives the system toward the conical intersection CI(S1/S0) region much faster. The proton-transferred TC excited state is not observed in the experiment due to a low instantaneous concentration. The back proton transfer occurring in the S0 state is barrierless according to calculations, so that it also probably has ultrafast character54. Thus, the evolution of transient spectra 0.8–100 ps (Fig. 5A) reflects vibrational cooling of the nascent hot TC species in the electronic ground state S0. The spectrally wide S1→TC absorption band in comparison to the vibrationally relaxed S0 TC absorption band is an expected feature55. The time-constant of vibrational cooling is 7.7 ps obtained from global fitting (Fig. 5B).

TC excited state deactivation in polar and hydrogen-bonding solvents. Upon changing from cyclohexane to methanol solution, the recorded transient absorption spectra are similar (Fig. S6), but the population of TC in the singlet excited state shows a longer lifetime (0.8 ps in methanol vs. 0.2 ps in cyclohexane, Table S3), suggesting ESIPT in that solvent, if present, is a minor deactivation path. Moreover, one would expect a slower ESIPT for 5-(OD)-NP in MeOD than for 5-(OH)-NP in MeOH, due to the difference in mass between deuterium and hydrogen, as reported in other molecular systems58,59. However, nearly identical transient absorption spectra and kinetics were collected for 5-(OD)-NP (in MeOD) and 5-(OH)-NP (in MeOH), which supports the hypothesis of minor ESIPT involvement in these solvents due to a high competition from internal conversion S1→S0 caused by a change in the TC S1 geometry in the C14=C1–C2=C3 bridge, by analogy with 5-(H)-NP58,59. In the polar acetonitrile, the transient absorption spectra for TC are similar to those in cyclohexane and methanol. The TC S1 state lifetime is 0.5 ps in acetonitrile (Fig. S7), thus longer than in cyclohexane (0.2 ps), but shorter in
relation to methanol (0.8 ps, Table S3). To rationalize the decrease of $\tau_{S1}$ in acetonitrile vs. methanol, we note that the TC $S_1$ state dipole moment is substantially high (Table 1). Thus, one expects that the high acetonitrile polarity exerts a stabilizing effect for TC in the excited state and $S_1 \rightarrow S_0$ internal conversion is facilitated. In methanol, on the other hand, strong solute–solvent specific interactions can slow down the geometry evolution needed for reaching the conical intersection, responsible for $S_1 \rightarrow S_0$ internal conversion. Interestingly, in acetonitrile and methanol, $\tau_{S1}$ TC * lifetimes are longer for 5-(OH)-NP than 5-(H)-NP (Table S3). The presence of the hydroxy group strengthens solute–solvent interactions, thereby hampering the change in TC * geometry.

Conclusions

Calculations in the gas phase show that the ESIPT process predominates in TC $S_1$ state deactivation over the TC $\rightarrow$ TT photosomization, hindering formation of the TT isomer. Internal conversion ($S_1 \rightarrow S_0$) may take place during the ESIPT process before the double-bond rotations are activated in the excited state. The ESIPT process is experimentally observed in cyclohexane by a shortening of the singlet excited TC lifetime to 0.2 ps in relation the unsubstituted compound (0.8 ps for 5-(H)-NP)24. Such fast dynamics of ESIPT has been reported in structurally related 3-hydroxycromone26. In other solvents, such as methanol or acetonitrile, ESIPT plays a less important role in TC excited state deactivation, since the intramolecular hydrogen bond is disrupted by solute–solvent specific interaction. The polar TC $S_1$ species is stabilized by solvent polarity, and the TC $S_1$ deactivation mainly occurs through the internal conversion process $S_1 \rightarrow S_0$ induced by a change in geometry upon activation of the two double bonds present in the $C_1=C_2=C_3=C_4$ bridge. Stabilization of TC $S_1$ species in polar solvent lowers the $S_1$-state potential-energy profile (vs. $S_0$-state), thus the conical intersection CI($S_1/S_0$) produces the $S_0$ state with less advanced change in the $C_1=C_2$ twist angle. Consequently, TT formation is disfavoured. On the other hand, different types of solvent-molecule interactions (dipole–dipole, π–π stacking and hydrogen bonding) slow down the TC * geometry evolution towards the conical intersection CI ($S_1/S_0$).

These main pathways (ESIPT or polarity-mediated IC) appear to reduce photosomization via the channel TC $\rightarrow$ TT. This explains the reduction of the TT population in the photochromic reaction using continuous UV irradiation performed for 5-(OH)-NP in comparison to the parent compound 5-(H)-NP. An unintended consequence of 5-hydroxy substitution is a weak residual color in 5-(OH)-NP solutions due to the presence of small quantities (ca. 1%) of the colored TC isomer produced through thermal equilibrium in cyclohexane solution. This is a result of the intramolecular hydrogen bond present in the structure, stabilizing its relative energy vs. the closed colorless form CF. Breaking the intramolecular hydrogen bond in methanol or acetonitrile by solute–solvent specific interactions shifts the equilibrium towards CF.

Data availability

The datasets generated during the current study are available from the corresponding author on request.

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**Author contributions**

The following co-authors contributed in particular with; B.G. synthesis, writing—review and editing, S.M., conceptualization, writing—review and editing, M.R. theoretical calculations, conceptualization, writing—review and editing and G.B. spectroscopic experiments, formal analysis, supervision, funding acquisition, conceptualization, writing—review and editing.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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