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Mechanochemical Reactivity of a Multimodal 2H-Bis-Naphthopyran Mechanophore

Skylar K. Osler, Molly E. McFadden, Tian Zeng, and Maxwell J. Robb*

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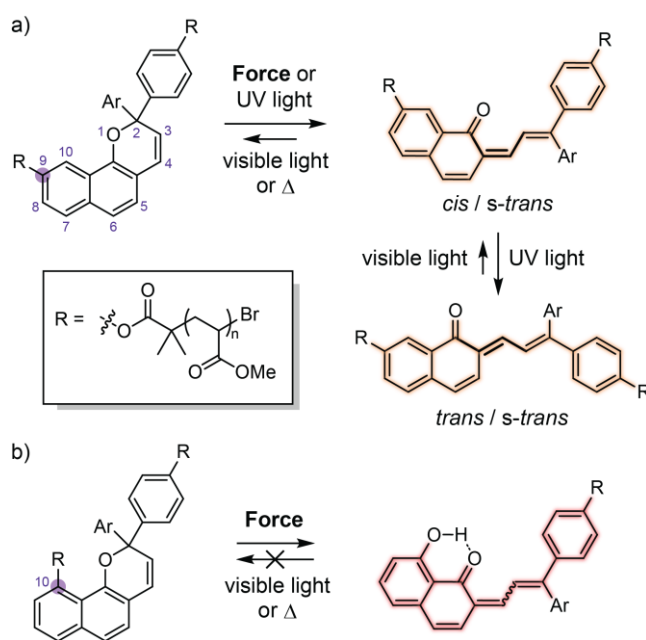
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Multimodal mechanophores that react under mechanical force to produce discrete product states with uniquely coupled absorption properties are interesting targets for the design of force-sensing polymers. Herein, we investigate the reactivity of a 2H-bis-naphthopyran mechanophore that generates thermally persistent mono-merocyanine and bis-merocyanine products upon mechanical activation in solution using ultrasonication, distinct from the thermally reversible products generated photochemically. We demonstrate that a force-mediated ester C(O)–O bond scission reaction following ring opening establishes an intramolecular hydrogen bond, locking one merocyanine subunit in the open form. Model compound studies suggest that this locked subunit confers remarkable thermal stability to bis-merocyanine isomers possessing a *trans* exocyclic alkene on the other subunit, implicating the formation of an unusual *trans* merocyanine isomer as the product of mechanochemical activation. Density functional theory calculations unexpectedly predict a thermally reversible retro-cyclization reaction of the bis-merocyanine species that could explain the mechanochemical generation of the unusual *trans* merocyanine isomer.

Introduction

Naphthopyrans are a class of molecular switches that undergo a ring-opening reaction upon photochemical or mechanochemical activation to generate a highly colored merocyanine dye. While the photochemical reactivity of naphthopyran has been studied extensively,¹ the mechanochemical reactivity of naphthopyran has only recently been investigated within the nascent field of polymer mechanochemistry.^{2–9} Mechanical force is transduced to naphthopyrans covalently incorporated into polymers by the application of stress to bulk materials,^{2–5} or by solution-phase ultrasonication,^{6–9} leading to merocyanine formation. Naphthopyran is thus a versatile mechanochromic force probe capable of reporting on stress and/or strain colorimetrically. Interestingly, the mechanochemical reactivity of naphthopyran mechanophores often diverges from their photochemical behavior.^{6,7,9}

Extended UV photoradiation of naphthopyrans generates a mixture of merocyanine isomers with *cis* and *trans* alkene geometry at the exocyclic olefin (Scheme 1a).^{10–19} Merocyanines with *trans* exocyclic olefin geometry are more thermally stable, while the *cis* isomers readily revert to the naphthopyran under ambient conditions. In contrast to the photochemical reactions, the thermal reversion behavior of most mechanochemically generated naphthopyran-derived merocyanines suggests that only the isomer with *cis* stereochemistry of the exocyclic alkene is produced using



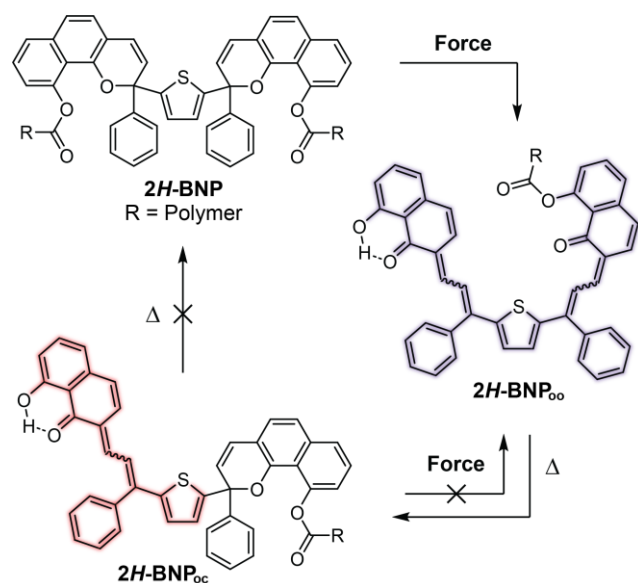
Scheme 1. Reactions of 2H-naphthopyran-containing poly(methyl acrylate) polymers and the structures of the merocyanine dyes produced upon mechanochemical or photochemical activation.

force.^{2–8} Recently, our group discovered a 2H-naphthopyran mechanophore scaffold that generates a persistent merocyanine dye after mechanical activation (Scheme 1b).⁷ Rather than *cis*–*trans* isomerization, a unique intramolecular hydrogen bonding mechanism is implicated in the persistent color generation whereby the scission of a C(O)–O ester bond

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

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Scheme 2. The anticipated mechanochemical reactivity of **2H-BNP** wherein mechanical force induces a dual ring-opening reaction accompanied by ester scission leading to a transient bis-merocyanine intermediate (**2H-BNP_{oo}**), which thermally reverts to form a stable mono-merocyanine dye (**2H-BNP_{oc}**).

following pyran ring opening establishes a β -hydroxy ketone that prevents merocyanine reversion.

Mechanochromic mechanophores possessing multiple reactive sites are theoretically capable of a more complex colorimetric response, accessing distinct states under mechanical force that are coupled to unique changes in optical properties.²⁰ For example, a bis-naphthopyran mechanophore previously developed in our group displays force-dependent multicolor mechanochromism due to a force-modified dynamic equilibrium that is established between two different merocyanine states.⁶ In contrast to the photochemical reaction, which proceeds via sequential ring-opening reactions of each pyran unit,^{21–24} mechanical activation was found to simultaneously open both pyran rings to generate the bis-merocyanine species. Because the mono-merocyanine product is formed via thermal reversion, increasing the amount of force applied to the mechanophore increases the rate of bis-merocyanine formation relative to mono-merocyanine and shifts the relative distribution of the two distinctly colored dyes. Naphthodipyran⁹ and diketopyrrolopyrrole^{25,26} mechanophores also display multicolor mechanochromism under force; however, the dyes produced from these mechanophores are either transient and revert to their original state after stress is removed, or require a trapping agent for persistent color generation. In bulk materials, spiropyran^{27,28} and rhodamine²⁹ mechanophores have been shown to generate uniquely colored states under active tension and after stress relaxation. Notably, mechanophores that display multicolor mechanochromism and generate persistent coloration remain limited.^{26,30}

We were interested in exploring the mechanochromism of a bis-naphthopyran mechanophore potentially capable of generating persistent coloration via the same intramolecular hydrogen bonding mechanism associated with the **2H**-naphthopyran mechanophore described above (Scheme 2). In

analogy to our previously studied **3H**-bis-naphthopyran mechanophore,⁶ we imagined that the two pyran rings of a **2H**-bis-naphthopyran (**2H-BNP**) mechanophore would open simultaneously upon ultrasound-induced mechanical activation to generate bis-merocyanine **2H-BNP_{oo}** (open–open), followed by rapid scission of a C(O)–O ester bond on one of the merocyanine units. This bond cleavage would position the mechanophore at the end of the polymer chain, precluding further mechanochemical reaction.³¹ The merocyanine unit with an intact ester linkage would be expected to undergo a thermal ring-closing reaction to produce persistent mono-merocyanine **2H-BNP_{oc}** (open–closed). Here, we study the mechanochemical reactivity of this **2H-BNP** mechanophore in dilute polymer solutions using ultrasonication. While mechanical activation results in the anticipated ring-opening reactions accompanied by ester cleavage, the reactivity is unexpectedly complex. A multifaceted experimental and computational approach provides insights into the unusual reactivity of this **2H-BNP** mechanophore.

Results and Discussion

We investigated the mechanochemical reactivity of the **2H-BNP** mechanophore through solution-phase ultrasonication experiments.^{31,32} Polymer attachment at the 10-position of each naphthopyran subunit is critical to form the persistent hydrogen-bonded merocyanine dye.⁷ Polymer **2H-BNP₁₀₉** ($M_n = 109$ kDa, $\bar{D} = 1.17$) was synthesized by a Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction between bis-alkyne **1a** and two equivalents of azide-terminated poly(methyl acrylate) (PMA) polymer **PMA-Azide** ($M_n = 59$ kDa, $\bar{D} = 1.10$) (Figure 1a).³³

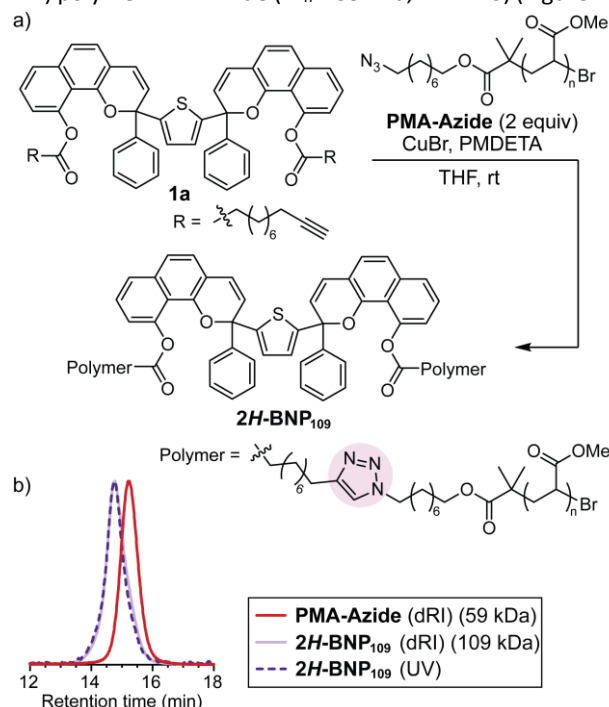


Figure 1. (a) Synthesis of a poly(methyl acrylate) polymer (109 kDa, $\bar{D} = 1.17$) containing a chain-centered **2H**-bis-naphthopyran mechanophore unit via CuAAC. (b) Characterization by GPC-MALS with differential refractive index (dRI) and in-line UV detection (345 nm) confirms **2H**-bis-naphthopyran functionalization near the chain center.

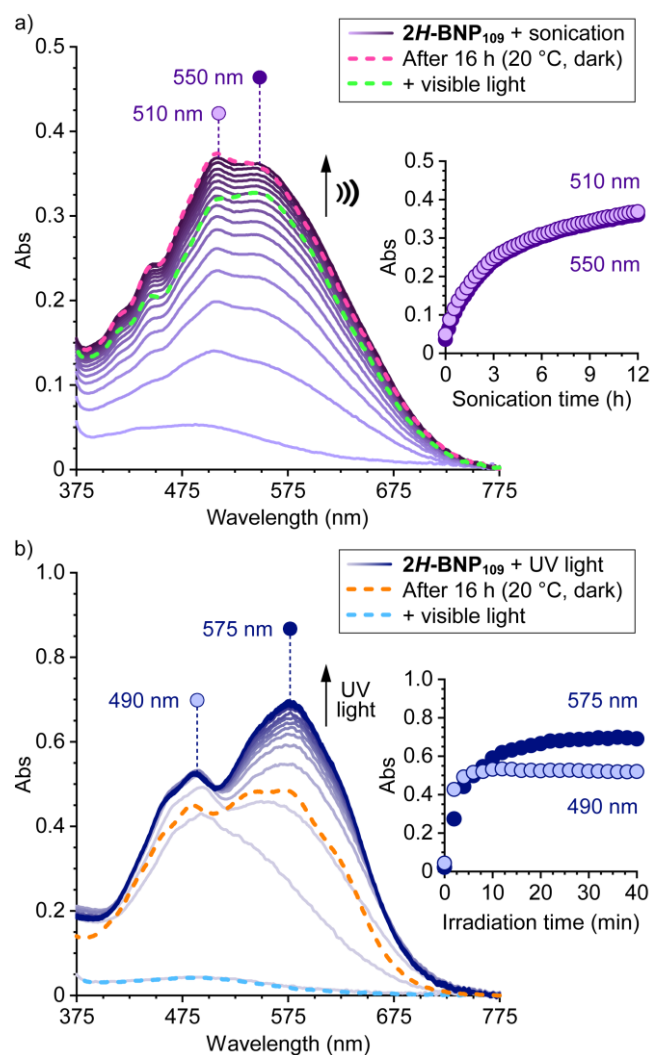


Figure 2. (a) Ultrasound-induced mechanochemical activation (12 h, 20 °C) of **2H-BNP₁₀₉** generates a product mixture with absorption maxima at approximately 510 and 550 nm. After incubation at 20 °C for 16 h in the dark, the spectrum remains essentially unchanged. Irradiation with 565 nm light (150 min) results in minimal bleaching. (b) Photoirradiation of **2H-BNP₁₀₉** with 365 nm UV light (40 min, 20 °C) generates a product mixture with absorption maxima at ~490 and 575 nm. Some attenuation of the absorbance is observed after 16 h in the dark (20 °C). Irradiation with 565 nm light (180 min) results in nearly complete bleaching. Insets show time-dependent absorbance at the specified wavelengths.

Characterization by GPC-MALS with in-line UV absorption detection confirmed that the **2H-BNP** mechanophore was incorporated near the chain-center where mechanical force is maximized (Figure 1b).^{31,34,35}

To investigate the mechanochemical activation of the **2H-BNP** mechanophore, a solution of **2H-BNP₁₀₉** (2 mg/mL in THF containing 30 mM BHT) maintained at ~20 °C was subjected to continuous ultrasonication (20 kHz, 8.2 W/cm²) for 12 h (see the ESI for details). Generation of colored merocyanine products was monitored by synchronous UV-vis absorption spectroscopy using a continuous flow setup.^{6,36} Ultrasound-induced mechanochemical activation of **2H-BNP₁₀₉** produces an absorption spectrum with two local maxima at 510 and 550 nm (Figure 2a). The absorption spectrum of the mechanochemical reaction products remains essentially unchanged 16 h after the

cessation of ultrasound, indicating that mechanical activation produces a thermally persistent merocyanine species. Extended irradiation with intense visible light (565 nm, 150 min) causes a slight attenuation of the absorption features, but does not induce significant bleaching (Figure S1), consistent with the formation of a permanent merocyanine dye locked via an intramolecular H-bonding interaction.⁷ To our surprise, however, even the longer wavelength absorption features attributed to the bis-merocyanine are largely persistent under these conditions, indicating the presence of an unusually stable bis-merocyanine species. Notably, the simultaneous cleavage of both C(O)–O ester linkages is unlikely. Thus, this persistent bis-merocyanine species likely contains a single intact ester group on one merocyanine subunit, consistent with the structure of **2H-BNP_∞** shown in Scheme 2. The slight attenuation of the absorption spectrum after irradiation with visible light is consistent with *trans*-to-*cis* isomerization of the exocyclic alkene in the merocyanine subunit containing the intramolecular H-bond (Figures S2 and S3, see the ESI for additional details).¹² Control experiments demonstrate that the absorption spectrum generated from photochemical activation of **2H-BNP₁₀₉** is distinct from the spectrum obtained during sonication experiments (Figure 2b and Figure S4). Furthermore, in contrast to the products of mechanochemical activation, the colored species produced under UV light undergo significant

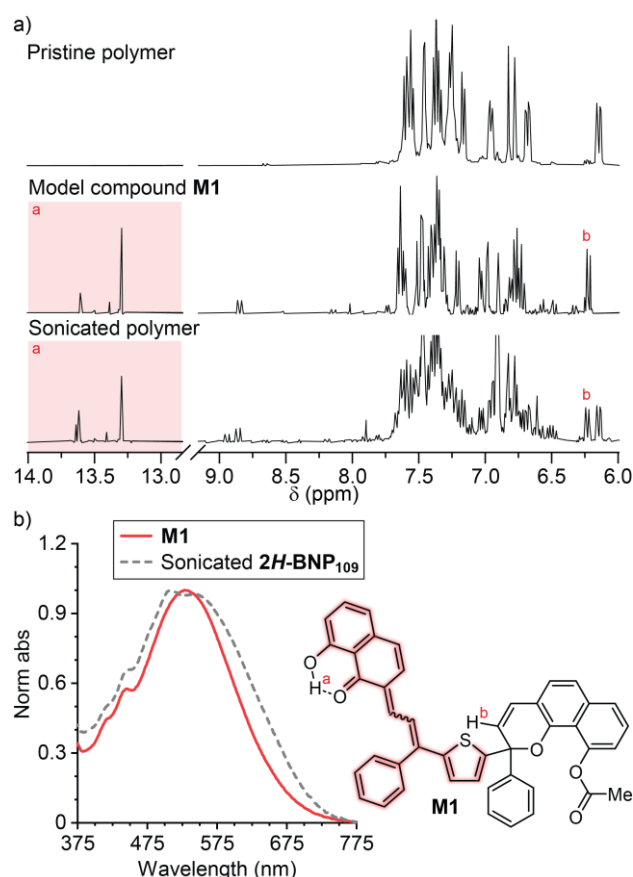


Figure 3. (a) Characteristic resonances in the ¹H NMR (THF-*d*₈, 400 MHz) spectrum of model compound **M1** are also observed in the product mixture generated from ultrasound-mediated mechanical activation of **2H-BNP₁₀₉**. (b) The absorption spectrum generated during the sonication of **2H-BNP₁₀₉** is not consistent with pristine **M1**. The long wavelength feature is bathochromically shifted from the absorption maximum of **M1**.

reversion under ambient conditions and completely revert to the colorless state upon irradiation with visible light. Together, these data suggest that the thermally persistent species produced upon ultrasound-induced mechanochemical activation of **2H-BNP**₁₀₉ are neither the expected mono-merocyanine locked by an intramolecular H-bond, nor the bis-merocyanine product with two intact ester linkages.

To identify the persistent mechanochemical product(s) of **2H-BNP**₁₀₉ activation, small molecule model compound **M1** was synthesized and characterized by ¹H NMR and UV-vis absorption spectroscopy (Figure 3). Consistent with prior studies of a related 2H-naphthopyran mechanophore,⁷ deprotection of the 10-hydroxyl group on the bis-naphthopyran precursor results in spontaneous thermal equilibration to the mono-merocyanine form. Characteristic proton resonances in the 13–14 ppm region of the ¹H NMR spectrum of **M1** are attributed to the hydrogen-bonded OH proton (H^b) on various merocyanine stereoisomers (Figure 3a). These diagnostic signals are also observed in the ¹H NMR spectrum of **2H-BNP**₁₀₉ after ultrasonication. The intact pyran ring on the naphthopyran subunit of **M1** is identified by a doublet at 6.40 ppm (H^b, *J* = 9.5 Hz). This resonance is also observed in the ¹H NMR spectrum of **2H-BNP**₁₀₉ after ultrasound-induced mechanical activation, along with a pair of overlapping doublets at 6.14 and 6.15 ppm (*J* = 9.6 Hz) corresponding to pyran protons of residual unreacted **2H-BNP**. While signatures of the mono-merocyanine species with a single β-hydroxy ketone motif are clearly visible in the ¹H NMR spectrum of **2H-BNP**₁₀₉ after ultrasonication, further analysis by NMR spectroscopy is obscured by overlapping peaks in the aromatic region. The UV-vis absorption spectrum of **M1** contains a single peak with a maximum at 530 nm, which is notably distinct from the spectrum obtained after mechanochemical activation of **2H-BNP**₁₀₉ (Figure 3b). The absorption spectrum acquired after sonication of **2H-BNP**₁₀₉ has an absorption edge that is bathochromically shifted from that

of **M1**, further suggesting that the sonication product mixture contains a persistent bis-merocyanine species with longer wavelength absorption in addition to mono-merocyanine isomers.

Further structural elucidation of the mechanochemical product mixture was achieved by photochemical activation of model compound **M1** to generate the bis-merocyanine species. A solution of **M1** (0.01 mg/mL in THF) was irradiated with UV light (365 nm, 8 min) at 20 °C using the same analytical flow setup as above (Figure 4a). Immediately following photoirradiation, the absorption spectrum exhibits two local maxima at 505 and 580 nm. This extended UV irradiation generates a substantial amount of bis-merocyanine, resulting in significant absorption in the longer wavelength region. However, after an extended period under ambient conditions in the dark (16 h, 20 °C), the absorption spectrum evolves to ultimately match that obtained from ultrasonication of polymer **2H-BNP**₁₀₉ (Figure 4a, inset). Partial retention of the longer wavelength absorption features suggests that photoirradiation of **M1** generates a mixture of thermally transient and thermally persistent bis-merocyanine isomers (Figure 4b). We identify the thermally transient bis-merocyanine species as having *cis* exocyclic alkene geometry on the merocyanine unit with an intact ester linkage at the 10-position (*cis*-**2H-BNP**_{oo}).¹⁸ The thermally persistent bis-merocyanine species is attributed to isomers with *trans* exocyclic alkene geometry on the merocyanine subunit with an intact ester linkage at the 10-position (*trans*-**2H-BNP**_{oo}). Increasing exposure of **M1** to UV light results in a greater proportion of thermally persistent *trans*-**2H-BNP**_{oo}, consistent with the expected photochemical *cis*-to-*trans* isomerization of the exocyclic alkene (Figure S5).^{18,19} Visible light irradiation is known to accelerate *trans*-to-*cis* isomerization, which must occur before electrocyclization to regenerate the naphthopyran.^{11,12,18,19} However, photochemical activation of **M1** produces products that do not

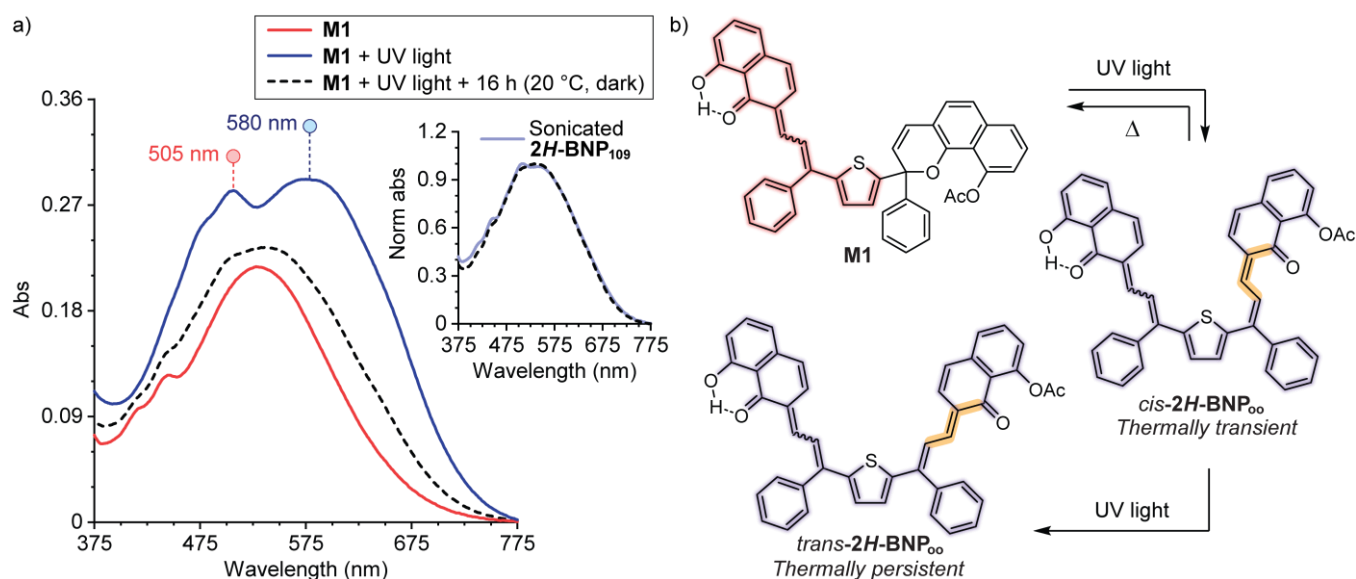


Figure 4. (a) Photoirradiation of **M1** with UV light (345 nm, 8 min) results in a bathochromic shift in absorption with maxima at 505 and 580 nm. Upon cessation of photoirradiation and 16 h in the dark (20 °C), the spectrum evolves to closely match the final absorption spectrum obtained upon sonication of **2H-BNP**₁₀₉ (inset). (b) Reaction scheme illustrating the formation of a mixture of thermally transient and persistent bis-merocyanine isomers with *cis* and *trans* exocyclic alkene geometry on the ester-containing subunit upon exposure of **M1** to UV light.

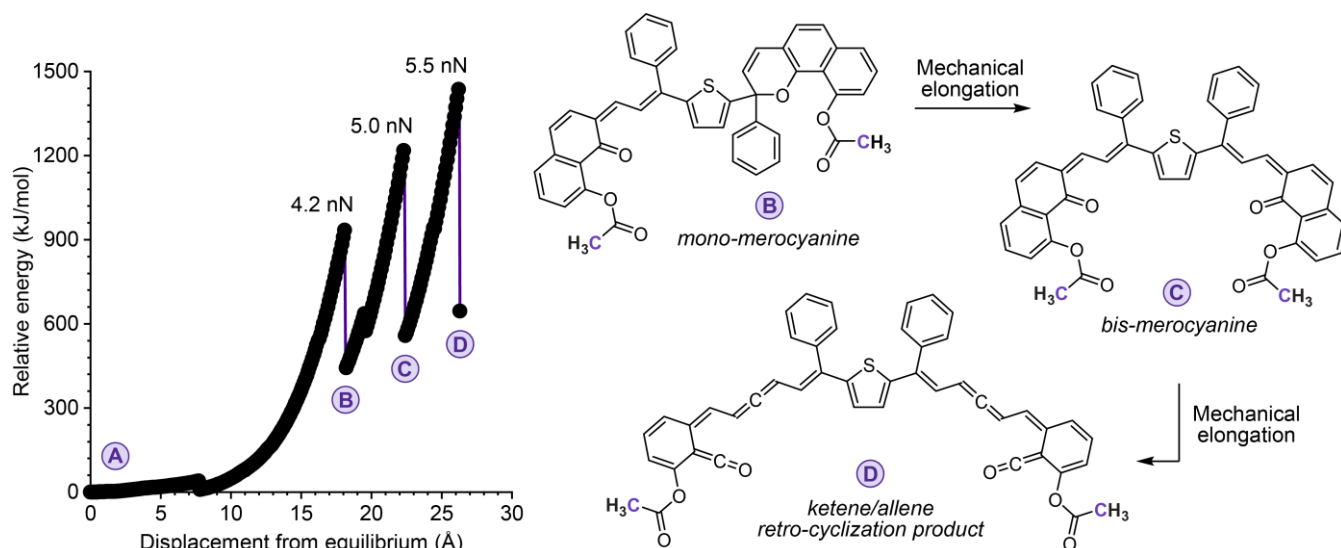


Figure 5. Density functional theory (DFT) calculations using the constrained geometries simulate external force (CoGEF) method performed on a truncated model of **2H-BNP** predict an unusual retro-cyclization reaction upon extended mechanical elongation to generate two sets of ketene and allene motifs. Structures are shown that correspond to the computed products of pyran ring opening (B and C) and the unusual retro-cyclization reaction (D) on the CoGEF profile. Calculations were performed at the B3LYP/6-31G* level of theory. The purple carbon atoms of the terminal methyl groups define the distance constraint.

bleach appreciably under visible light, similar to the mechanochemically-generated products of **2H-BNP**₁₀₉ (Figure S6). On the other hand, complete reversion of photochemically produced merocyanines is possible using visible light when both ester linkages at the 10-position are intact (Figure 2b). These results suggest that the unique persistence of *trans*-**2H-BNP**_∞ relies on having one merocyanine subunit locked in the open form via the intramolecular hydrogen bond.

The results presented above indicate that the photochemical activation of **M1** and the mechanochemical activation of **2H-BNP**₁₀₉ generate similar product mixtures. An important implication is that the mechanochemical ring-opening reaction of the *2H*-BNP mechanophore produces a mixture of bis-merocyanine isomers with both *cis* and *trans* geometry of the exocyclic alkene on the merocyanine subunit with an intact ester linkage at the 10-position. For typical naphthopyran-derived merocyanines, thermal *cis*-to-*trans* isomerization of the exocyclic alkene is rare.^{16,19} As discussed above, the mechanochemical generation of merocyanines with a *trans* exocyclic olefin is unusual from naphthopyran mechanophores. Consistent with the mechanical activation of **2H-BNP**₁₀₉, sonication experiments performed on analogous polymers with lower (**2H-BNP**₄₄: $M_n = 44$ kDa, $\bar{D} = 1.25$) and higher (**2H-BNP**₃₁₇: $M_n = 317$ kDa, $\bar{D} = 1.17$) molar mass result in product mixtures with similar absorption maxima at 510 and 550 nm, suggesting that the ratio of mechanically-generated *cis* and *trans* merocyanine products is not force-dependent (Figure S7 and S8).³⁷ Notably, low-temperature sonication of **2H-BNP**₃₁₇ results in the detectable accumulation of a thermally transient bis-merocyanine species due to the increased reaction rate,³⁶ confirming that mechanical activation of *2H*-BNP does generate *cis*-**2H-BNP**_∞ in addition to the thermally persistent *trans* isomers analogous to the photochemical pathway illustrated in Figure 4b (Figure S9).

Density functional theory (DFT) calculations using the constrained geometries simulate external force (CoGEF) method^{38,39} performed on a truncated model offer an intriguing explanation for the unique mechanochemical generation of merocyanine isomers from *2H*-BNP that possess a *trans* alkene in the ester-containing subunit (Figure 5). Molecular elongation first results in the expected ring-opening reactions to form the bis-merocyanine product; however, extended elongation does not result in the C(O)–O ester bond scission that was observed previously for the analogous *2H*-naphthopyran.⁷ Instead, a retro-cyclization reaction is predicted to occur simultaneously on both merocyanine subunits to generate two sets of ketene and allene moieties. Electrocyclic ketene-forming reactions have been reported under thermal⁴⁰ and photochemical^{41,42} conditions, providing some precedent for this unusual transformation. If such a retro-cyclization reaction occurs in practice, the species would be predicted to undergo rapid thermal cyclization⁴² upon chain relaxation to regenerate a mixture of merocyanines with *cis* and *trans* exocyclic alkene geometry. Notably, this unusual retro-cyclization reaction is not predicted by CoGEF for a *2H*-BNP model with ester groups at the 9-position of the two naphthopyran subunits (Figure S10). Consistent with these computational predictions, ultrasonication experiments performed on a polymer containing a chain-centered *2H*-BNP mechanophore connected at the 9-position via ester linkages on each subunit does not generate any thermally persistent merocyanine isomers (Figure S11).

Conclusions

In summary, we have investigated the mechanochemical reactivity of a *2H*-bis-naphthopyran mechanophore (*2H*-BNP). Instead of the expected force-dependent multicolor mechanochromism, which is predicated on a dynamic equilibrium involving the thermal reversion of the bis-

merocyanine product,⁶ we find that ultrasound-induced mechanochemical activation of 2H-BNP results in an unexpectedly persistent bis-merocyanine species. Scission of a C(O)–O ester bond at the 10-position on one naphthopyran subunit establishes an intramolecular hydrogen bond that locks one merocyanine subunit open. In contrast to previously reported naphthopyran mechanophores that appear to exclusively produce the *cis* merocyanine product upon ring opening, mechanical activation of 2H-BNP generates a mixture of merocyanine isomers with *cis* and *trans* geometry of the exocyclic alkene on the merocyanine subunit with an intact ester linkage. Supported by small molecule model studies, the bis-merocyanine isomers with a *trans* exocyclic alkene on the ester-containing subunit are thermally persistent and resist bleaching under visible light irradiation. Density functional calculations implicate an unusual, thermally reversible mechanochemical retro-cyclization reaction of the bis-merocyanine species that is plausibly responsible for the formation of the *trans* merocyanine isomer, rather than a direct mechanically facilitated *cis*-to-*trans* isomerization. Efforts within our group are currently underway to experimentally probe the possibility of this unusual transformation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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