Supplementary Information for

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

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I. General Experimental Details

Reagents from commercial sources were used without further purification unless otherwise stated. Methyl acrylate was passed through a short plug of basic alumina to remove inhibitor immediately prior to use. Copper wire was soaked in 1 M HCl for 10 min and then rinsed consecutively with water, acetone, and dichloromethane immediately prior to use. Dry THF was obtained from a Pure Process Technology solvent purification system. All reactions were performed under a N₂ atmosphere unless specified otherwise. Column chromatography was performed on a Biotage Isolera system using SiliCycle SiliaSep HP flash cartridges.

NMR spectra were recorded using either a 400 MHz Bruker Avance III HD with Prodigy Cryoprobe or a 600 MHz Varian spectrometer with 5 mm triple resonance inverse probe. All ¹H NMR spectra are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), acetone (2.05 ppm), dichloromethane (5.32 ppm), THF (3.58 ppm), or benzene (7.16 ppm) in deuterated solvent. All ¹³C NMR spectra were measured in deuterated solvents and are reported in ppm relative to the signals for chloroform (77.16 ppm), acetone (206.26 ppm), or dichloromethane (53.84 ppm). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, app = apparent.

High resolution mass spectra (HRMS) were obtained from a Waters Corp. LCT Premier XE time-of-flight mass spectrometer equipped with an electrospray ionization (ESI) probe, a JEOL JMS-600H magnetic sector mass spectrometer equipped with a FAB+ probe, or via direct injection on an Agilent 1260 Infinity II Series HPLC coupled to a 6230 LC/TOF system in electrospray ionization (ESI+) mode.

Analytical gel permeation chromatography (GPC) was performed using an Agilent 1260 series pump equipped with two Agilent PLgel MIXED-B columns (7.5 x 300 mm), an Agilent 1200 series diode array detector, a Wyatt 18-angle DAWN HELEOS light scattering detector, and a Optilab rEX differential refractive index detector. The mobile phase was THF at a flow rate of 1 mL/min. Molecular weights and molecular weight distributions were calculated by light scattering using a dn/dc value of 0.062 mL/g (25 °C) for poly(methyl acrylate).

UV-vis absorption spectra were recorded on a Thermo Scientific Evolution 220 spectrometer.

Ultrasound experiments were performed using a Vibra Cell 505 liquid processor equipped with a 0.5-inch diameter solid probe (part #630-0217), sonochemical adapter (part #830-00014), and a Suslick reaction vessel made by the Caltech glass shop (analogous to vessel #830-00014 from Sonics and Materials). Polymer solutions were continuously sampled for UV-vis analysis using a Cole Parmer Masterflex L/S pump system (item #EW-77912-10) composed of an L/S pump head (part #77390-00) and L/S precision variable speed drive (part #07528-20) using 4x6 mm PTFE tubing (part #77390-60) and a quartz flow-through cell (Starna, part #583.4-Q-10/Z8.5), which was connected using M6-threaded PTFE tubing (Starna, part #M6-SET). Either an ice bath or a Thermo Scientific EK45 Immersion Cooler (part #3281452) was used to maintain a constant temperature bath for sonication experiments. Photoirradiation with UV light was performed using either a DR/9W-UVA 365 nm lamp or a Philips PL-S 9W/01/2P UVB bulb with a narrow emission of 305–315 nm and a peak at 311 nm under ambient conditions unless indicated otherwise. Irradiation with yellow-green light filtered through a 425 nm bandpass filter was applied to sample solutions using a 565 nm LED (ThorLabs M565L3), driver (ledd1B), and collimator (SM1U25-A).

Compounds Mono-M1 and 5c were synthesized following the procedures reported in the literature.¹

II. Supplementary Figures



Figure S1. Photoirradiation (565 nm visible light) of the final product mixture resulting from mechanochemical activation of **2H-BNP**₁₀₉ produces minimal bleaching. See Section VII for experimental details.



Figure S2. (a) Photoirradiation of **Mono-M1** for varying amounts of time with 311 nm UV light results in a different distribution of *cis* and *trans* merocyanine isomers with respect to the exocyclic alkene, as evidenced by (b) ¹H NMR (600 MHz, THF-*d*₈) and (c) UV-vis absorption spectroscopy. There is a linear relationship between the percent *cis* configuration at the exocyclic alkene determined by ¹H NMR spectroscopy and the wavelength of the absorption maximum (inset). See Section VIII for details.



Figure S3. UV-vis absorption spectra measured in a sealed cuvette upon varying exposure of a solution of **Mono-M1** (10 μ M, THF) to 311 nm UV light. The relative amount of *cis* and *trans* merocyanine isomers was determined using the calibration curve in Figure S2. An increase in the relative amount of the *trans* merocyanine isomer is coupled to a hypsochromic shift in λ_{max} and an increase in absorbance due to the higher absorptivity of the *trans* merocyanine isomer. See Section VIII for details.



Figure S4. UV-vis absorption spectra measured in the flow setup (a) during photoirradiation using 365 nm UV light (40 min) of polymer **2H-BNP**₁₀₉ (2 mg/mL in THF, 20 °C) and (b) following cessation of photoirradiation in the dark (20 °C, 18 hours). (c) Photoirradiation of the residual thermally persistent product with 565 nm visible light (180 min) results in nearly complete bleaching.



Figure S5. UV-vis absorption spectra measured after exposure of three separate solutions of **M1** (0.01 mg/mL in THF, 20 °C) to 365 nm UV light for (a) 2 min, (b) 8 min, or (c) 20 min in the continuous flow setup. Longer exposure to UV light is correlated with a bathochromic shift in the final absorption spectrum following a period in the dark (16 h, 20 °C), indicating the generation of increasing amounts of thermally stable bis-merocyanine isomers.



Figure S6. Photoirradiation (565 nm visible light) of the final product mixture resulting from photochemical activation of **M1** (365 nm UV light, 8 min) produces minimal bleaching. See section VII for details.



Figure S7. (a) Absorption spectra acquired during ultrasound-induced mechanochemical activation of polymer **2H-BNP**₄₄ with $M_n = 44$ kDa (24 h sonication at -15 °C, 2 mg/mL in THF containing 30 mM BHT). (b) Photoirradiation of the final mechanochemical product mixture with 565 nm visible light results in minimal bleaching. See section VII for details.



Figure S8. (a) Absorption spectra acquired during ultrasound-induced mechanochemical activation of polymer **2H-BNP**₃₁₇ with $M_n = 317$ kDa (2 h sonication at 20 °C, 2 mg/mL in THF containing 30 mM BHT). (b) Photoirradiation of the final mechanochemical product mixture with 565 nm visible light results in minimal bleaching. See section VII for details.



Figure S9. (a) Absorption spectra acquired during ultrasound-induced mechanochemical activation of **2H-BNP**₃₁₇ (25 min sonication at -15 °C, 2 mg/mL in THF containing 30 mM BHT). (b) UV-vis absorption spectra measured after cessation of sonication illustrating a slight attenuation of absorbance and a hypsochromic shift of the peak maximum from 580 to 550 nm. See section VII for details.



Figure S10. Density functional theory (DFT) calculations using the constrained geometries simulate external force (CoGEF) method performed on a truncated model of an analog of the 2*H*-BNP mechanophore with attachment points at the 9-position of each naphthopyran subunit instead of the 10-position. Computed structures are shown at right that correspond to the indicated points in the CoGEF profile along with the associated constraint distance between the terminal methyl groups (pink carbon atoms designate the anchor points defining the distance constraint). The first and second ring-opening reactions are predicted to occur at a maximum force of 4.0 and 4.4 nN, respectively. Scission of a C–C(O) bond of one of the ester groups is predicted to occur with a force of 6.0 nN. Calculations were performed at the B3LYP/6-31G* level of theory.



Figure S11. (a) UV-vis absorption spectra acquired during ultrasound-induced mechanochemical activation of control polymer (9)-2H-BNP₁₀₄ (75 min sonication at -15 °C, 2 mg/mL in THF containing 30 mM BHT). Polymer (9)-2H-BNP₁₀₄ contains polymer attachment points at the 9-position of each naphthopyran subunit. (b) Time-dependent absorbance at 500 nm acquired after cessation of sonication illustrating nearly complete reversion of the mechanically generated merocyanine species, in contrast to the thermally persistent species produced upon mechanical activation of the 2H-BNP mechanophore with polymer attachment at the 10-position of each naphthopyran subunit.

III. Synthetic Details



2,2'-Thiobis(1-phenylethan-1-one) (2). A 250 mL two-neck round bottom flask equipped with a stir bar was charged with 2-bromo-1-phenylethan-1-one (11.5 g, 57.8 mmol). The flask was evacuated and backfilled with N_2 (2x), followed by the addition of acetone (125

mL). The solution was cooled to 0 °C in an ice bath and sodium sulfide nonahydrate (7.0 g, 29.0 mmol) in deionized water (15 mL) was added slowly via syringe. The reaction was stirred at 0 °C for 1 h, then warmed to room temperature and stirred for 16 h. The reaction mixture was concentrated under reduced pressure and the resulting aqueous solution was washed with dichloromethane (3 x 150 mL). The organic layers were combined, dried over MgSO₄, filtered, and concentrated. The crude material was purified by column chromatography on silica gel (30% EtOAc/hexanes) and subsequently recrystallized from dichloromethane/hexanes to provide the title compound as a pale tan crystalline powder (3.15 g, 40%).

¹H NMR (400 MHz, CDCl₃) δ: 8.02 – 7.92 (m, 4H), 7.63 – 7.54 (m, 2H), 7.51 – 7.44 (m, 4H), 3.99 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ: 194.3, 135.5, 133.7, 128.9, 128.8, 37.7.

TLC (25% EtOAc/hexanes): R_f = 0.50

HRMS (ESI m/z): calcd for $[C_{16}H_{15}O_2S]^+$ (M+H)⁺, 271.0793; found 271.0792.

Thiophene-2,5-diylbis(phenylmethanone) (3). A flame-dried 100 mL two-neck round bottom flask equipped with a stir bar and condenser was charged with 2,3-dihydroxy-1,4dioxane (460 g, 3.83 mmol). The flask was evacuated and backfilled with N₂ (3x), followed by the addition of anhydrous methanol (20 mL). The mixture was heated to reflux for 2 h to generate glyoxal. A separate flame-dried 50 mL round bottom flask equipped with a stir bar was charged with sodium metal (0.170 g, 7.40 mmol) and evacuated/backfilled with N₂ (3x). The flask was cooled to 0 °C in an ice bath and anhydrous methanol (8.5 mL) was added via syringe to form sodium methoxide. The flask containing glyoxal was removed from the heating bath and compound 2 (1.67 g, 6.18 mmol) in anhydrous dichloromethane (5 mL) was added under nitrogen to the warm glyoxal solution via syringe, followed by the dropwise addition of the sodium methoxide solution by syringe. The reaction mixture was returned to reflux (turning dark red) and stirred for 18 h. The reaction was cooled to room temperature, concentrated under reduced pressure, and dissolved in EtOAc (250 mL). The organic layer was washed consecutively with 1 M aqueous HCl (100 mL), deionized water (100 mL), saturated aqueous NaHCO₃ (100 mL), 1 M aqueous NaOH (100 mL), and brine (100 mL). The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column gel (5–40% EtOAc/hexanes) and subsequently chromatography on silica recrystallized from dichloromethane/hexanes to provide the title compound as off-white crystalline powder (0.879 g, 49%).

¹H NMR (400 MHz, CDCl₃) δ: 7.94 – 7.89 (m, 4H), 7.68 (s, 2H), 7.67 – 7.61 (m, 2H), 7.56 – 7.50 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ: 188.2, 148.6, 137.4, 133.9, 133.1, 129.5, 128.8.

TLC (25% EtOAc/hexanes): Rf = 0.58

HRMS (ESI m/z): calcd for $[C_{18}H_{13}O_2S]^+$ (M+H)⁺, 293.0636; found 293.0631.



1,1'-(Thiophene-2,5-diyl)bis(1-phenylprop-2-yn-1-ol) (4). A flame-dried 500 mL two-neck round bottom flask equipped with a stir bar was evacuated/backfilled with N_2 (3x) and charged with anhydrous THF (50 mL) and ethynyltrimethylsilane (2.84 mL, 20.5 mmol). The

flask was cooled to 0 °C in an ice bath and n-butyllithium (2.5 M in hexanes, 7.92 mL, 19.8 mmol) was added dropwise via syringe. The reaction was stirred at 0 °C for 80 min. Compound **3** (2.067 g, 7.07 mmol) in anhydrous THF (30 mL) was added to the reaction mixture via syringe under N₂. The reaction was stirred at 0 °C for 1 h, and then allowed to warm to room temperature. After stirring for 18 h, the solution was cooled to 0 °C in an ice bath and methanol (40 mL) was added to the reaction mixture. The reaction was warmed to room temperature and stirred for 8 h. The reaction mixture was cooled to 0 °C in an ice bath, neutralized by the slow addition of 1 M aqueous HCl, and extracted into EtOAc (300 mL). The organic layer was washed with deionized water (100 mL), saturated aqueous NH₄Cl (300 mL), saturated aqueous NaHCO₃ (2 x 300 mL), and brine (150 mL). The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (5–40% EtOAc/hexanes) to give the title compound (mixture of diastereomers) as a colorless crystalline solid (2.22 g, 91%).

¹H NMR (400 MHz, CDCl₃) δ: 7.68 (dt, J = 8.0, 1.6 Hz, 4H), 7.39 – 7.28 (m, 6H), 6.89 (s, 1H), 6.85 (s, 1H), 2.95 (s, 2H), 2.86 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ: 150.1, 150.0, 143.4, 143.3, 128.46, 128.45, 128.42, 125.84, 125.78, 125.1, 125.0, 85.6, 85.5, 75.31, 75.28, 71.88, 71.86.

TLC (25% EtOAc/hexanes): R_f = 0.32

HRMS (ESI *m/z*): calcd for [C₂₂H₁₇O₂S]⁺ (M–OH)⁺, 327.0838; found 327.0865.

10-Undecynoic anhydride. A flame-dried 100 mL two-neck round bottom flask equipped with a stir was charged with N,N'-dicyclohexylcarbodiimide (2.95 g, 14.3 mmol) and evacuated/backfilled with N₂ (3x). Anhydrous dichloromethane (25 mL) was added to the flask. A solution of 10undecynoic acid (5.11 g, 28.0 mmol) in anhydrous dichloromethane (25 mL) under N₂ was added to the reaction flask via syringe. The reaction was stirred at room temperature for 24 h, filtered through a glass frit, and concentrated under reduced pressure to give the title compound as a white solid (4.81 g, 99%). The crude material was carried forward without further purification.

<u>Crude ¹H NMR (400 MHz, Acetone) δ</u>: 2.51 (t, *J* = 7.3 Hz, 4H), 2.30 (t, *J* = 2.7 Hz, 2H), 2.17 (td, *J* = 7.0, 2.7 Hz, 4H), 1.69 – 1.28 (m, 24H).

<u>Crude ¹³C NMR (101 MHz, CDCl₃) δ:</u> 169.7, 84.8, 68.3, 35.4, 29.2, 29.0, 28.9, 28.7, 28.5, 24.3, 18.5.

HRMS (FD *m*/*z*): calcd for [C₂₂H₃₅O₃]⁺ (M+H)⁺, 347.2586; found 347.2582.



8-hydroxynaphthalen-1-yl undec-10-ynoate (5a). A flame-dried 250 mL two-neck round bottom flask equipped with a stir bar was charged with 1,8-dihydroxynaphthalene (2.24 g, 14.0 mmol) and 4-dimethylaminopyridine (0.171 g, 1.40 mmol). The flask was evacuated/backfilled with N₂ (3x), and anhydrous THF (50 mL) was added. Triethylamine (2.55 mL, 18.3 mmol) was added via syringe, and then the solution was cooled to 0 °C in an ice bath. A solution of 10-undecynoic

anhydride (4.85 g, 14.0 mmol) in anhydrous THF (50 mL) was added dropwise over 30 minutes under N₂. The reaction was warmed to room temperature and stirred for 16 h. The reaction was diluted with EtOAc (400 mL) and the organic layer was washed with saturated aqueous NH₄Cl (3 x 300 mL), saturated aqueous NaHCO₃ (300 mL), and brine (300 mL). The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (0–25% EtOAc/hexanes) and subsequently recrystallized from dichloromethane/hexanes to give the product as a colorless crystalline solid (2.80 g, 62%).

 $\frac{1}{H \text{ NMR (400 MHz, CDCl}_3) \delta:}{1.69 (dd, J = 8.3, 1.1 Hz, 1H), 7.43 - 7.28 (m, 4H), 7.18 (dd, J = 7.6, 1.1 Hz, 1H), 6.88 (dd, J = 7.5, 1.2 Hz, 1H), 2.69 (t, J = 7.5 Hz, 2H), 2.20 (td, J = 7.0, 2.6 Hz, 2H), 1.95 (t, J = 2.6 Hz, 1H), 1.81 (p, J = 7.5 Hz, 2H), 1.59 - 1.50 (m, 2H), 1.48 - 1.31 (m, 8H).$

¹³C NMR (101 MHz, CDCl₃) δ: 171.2, 152.0, 146.0, 137.0, 127.2, 126.5, 125.5, 120.4, 118.5, 117.0, 111.5, 84.9, 68.3, 34.8, 29.2, 29.1, 29.0, 28.8, 28.5, 24.8, 18.5.

TLC (25% EtOAc/hexanes): Rf = 0.50

HRMS (ESI *m/z*): calcd for [C₂₁H₂₃O₃]⁻ (M–H)⁻, 323.1653; found 323.1648.



8-hydroxynaphthalen-2-yl undec-10-ynoate (5b). A flame-dried 250 mL two-neck round bottom flask equipped with a stir bar was charged with 1,7-dihydroxynaphthalene (2.18 g, 13.6 mmol) and 4-dimethylaminopyridine (0.170 g, 1.39 mmol). The flask was evacuated/backfilled with N_2 (3x), and anhydrous THF (50 mL) was added. Triethylamine (2.50 mL, 17.9 mmol) was

added via syringe, and then the solution was cooled to 0 °C in an ice bath. A solution of 10-undecynoic anhydride (4.70 g, 13.6 mmol) in anhydrous THF (50 mL) was added dropwise over 30 minutes under N₂. The reaction was warmed to room temperature and stirred for 16 h. The reaction was diluted with EtOAc (400 mL) and the organic layer was washed with saturated aqueous NH₄Cl (3 x 300 mL), saturated aqueous NaHCO₃ (300 mL), and brine (300 mL). The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (0–55% EtOAc + 1% triethylamine/hexanes) to give the product as a pale pink solid (0.568 mg, 13%).

 $\frac{1}{14}$ NMR (400 MHz, CDCl₃) δ: 7.85 (d, J = 2.4 Hz, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.35 (d, J = 8.3 Hz, 1H), 7.22 – 7.15 (m, 2H), 6.68 (d, J = 7.5 Hz, 1H), 5.77 (s, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.20 (td, J = 7.1, 2.7 Hz, 2H), 1.96 (t, J = 2.7 Hz, 1H), 1.81 (p, J = 7.5 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.47 – 1.33 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ: 173.3, 151.4, 147.9, 132.8, 129.3, 125.7, 124.9, 121.7, 120.3, 113.4, 109.2, 84.9, 68.3, 34.6, 29.3, 29.2, 29.0, 28.8, 28.6, 25.1, 18.5.

TLC (25% EtOAc/hexanes): R_f = 0.47

HRMS (ESI *m*/*z*): calcd for [C₂₁H₂₃O₃]⁻ (M–H)⁻, 323.1653; found 323.1654.

General Procedure A for the Synthesis of Bis-naphthopyrans. Bis-naphthopyrans were synthesized according to the literature² following the general procedure developed by Zhao and Carreira.^{3,4} To a flame-dried two-neck round bottom flask equipped with a stir bar and reflux condenser was added bis-propargyl alcohol **4**, the appropriate naphthol, and a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS). The flask was evacuated and backfilled with N₂ (3x) followed by the sequential addition of 1,2-dichloroethane and trimethyl orthoformate via syringe. The reaction was heated to reflux and stirred for the indicated amount of time. Upon completion, the reaction was cooled to room temperature, concentrated with celite, and purified by column chromatography on silica gel.



Thiophene-2,5-diylbis(2-phenyl-2H-benzo[*h*]chromene-2,10-diyl) bis(undec-10-ynoate) (1a). Synthesized according to General Procedure A with compound 4 (0.400 g, 1.16 mmol), compound 5a (0.870 g, 2.68 mmol), PPTS (0.032 g, 0.127 mmol), 1,2-dichloroethane (10 mL), and trimethyl orthoformate (0.57 mL, 5.2 mmol). The reaction was stirred at reflux for 1.75 h. Purification by

column chromatography on silica gel (0–15% Et_2O/CH_2Cl_2 :hexanes (1:1)), followed by a second chromatographic separation on silica gel (0–40% EtOAc + 1% triethylamine/hexanes) afforded the title compound (mixture of diastereomers) as a dark red oil (0.195 g, 18%). We note that later column fractions were contaminated with the mono-merocyanine species, which was characterized by its reversion behavior under visible light irradiation to regenerate bis-naphthopyran **1a** (see Figure S12 below).

<u>¹H NMR (400 MHz, C₆D₆) δ</u>: 7.67 – 7.60 (m, 4H), 7.30 – 7.24 (m, 2H), 7.13 – 7.07 (m, 4H), 7.07 – 6.99 (m, 8H), 6.93 (s, 1H), 6.88 (s, 1H), 6.74 (dd, J = 8.3, 5.4 Hz, 2H), 6.20 (d, J = 9.6, 1H), 6.18 (d, J = 9.6, 1H), 5.81 (d, J = 9.6 Hz, 1H), 5.76 (d, J = 9.6 Hz, 1H), 2.25 – 2.06 (m, 4H), 2.03 – 1.96 (m, 4H), 1.84 – 1.80 (m, 2H), 1.53 – 1.42 (m, 4H), 1.41 – 1.31 (m, 4H), 1.29 – 1.18 (m, 4H), 1.13 – 1.01 (m, 12H).

¹³C NMR (101 MHz, Acetone) δ: 173.1, 173.0, 150.9, 150.7, 147.98, 147.96, 147.69, 147.67, 145.1, 144.9, 138.0, 137.9, 128.97, 128.95, 128.91, 128.89, 128.6, 127.6, 127.3, 127.2, 127.06, 127.05, 126.2, 124.8, 124.7, 122.4, 121.2, 120.1, 117.9, 117.8, 85.0, 82.4, 82.3, 69.9, 34.49, 34.47, 29.93, 29.90, 29.72, 29.71, 29.68, 29.4, 29.33, 29.32, 25.2, 18.8.

TLC (25% EtOAc/hexanes): R_f = 0.53

HRMS (ESI *m*/*z*): calcd for [C₆₄H₆₁O₆S]⁺ (M+H)⁺, 957.4183; found 957.4217.



Thiophene-2,5-diylbis(2-phenyl-2*H*-benzo[*h*]chromene-2,9-diyl) bis(undec-10-ynoate) (1b). Synthesized according to General Procedure A with compound 4 (0.145 g, 0.421 mmol), compound 5b (0.328 g, 1.01 mmol), PPTS (0.012 g, 0.048 mmol), 1,2dichloroethane (5 mL), and trimethyl orthoformate (0.21 mL, 1.9

mmol). The reaction was stirred at reflux for 2 h. Purification by column chromatography on silica gel (0–15% Et_2O/CH_2Cl_2 :hexanes (1:1)), followed by a second chromatographic separation on silica gel (0–40% EtOAc + 1% triethylamine/hexanes) afforded the title compound (mixture of diastereomers) as a dark red oil (0.022 g, 5.5%).

¹<u>H NMR (400 MHz, Acetone) δ</u>: 7.95 (ddd, J = 8.8, 2.3, 1.2 Hz, 2H), 7.83 (dd, J = 8.9, 1.8 Hz, 2H), 7.62 – 7.57 (m, 4H), 7.44 (ddd, J = 8.5, 2.7, 0.8 Hz, 2H), 7.35 – 7.22 (m, 10H), 6.84 – 6.79 (m, 4H), 6.39 (d, J = 9.7 Hz, 1H), 6.38 (d, J = 9.7 Hz, 1H), 2.63 (t, J = 7.5 Hz, 4H), 2.31 (t, J = 2.7 Hz, 2H), 2.16 (td, J = 6.9, 2.8 Hz, 4H), 1.79 – 1.69 (m, 4H), 1.55 – 1.32 (m, 20H).

¹³C NMR (101 MHz, CD₂Cl₂) δ: 172.7, 150.73, 150.70, 149.20, 149.18, 147.41, 147.39, 144.33, 144.31, 133.0, 129.47, 129.46, 128.6, 128.37, 128.35, 127.71, 127.68, 126.5, 126.1, 126.0, 125.3, 124.7, 124.30, 124.27, 122.47, 122.45, 121.15, 121.12, 116.4, 116.3, 113.28, 113.25, 85.1, 81.6, 81.5, 68.3, 34.7, 29.55, 29.50, 29.48, 29.47, 29.39, 29.33, 29.1, 28.9, 25.2, 18.7.

TLC (25% EtOAc/hexanes): R_f = 0.58

HRMS: calcd for [C₆₄H₆₁O₆S]⁺ (M+H)⁺, 957.4183; found 957.4197.



Thiophene-2,5-diylbis(2-phenyl-2H-benzo[*h*]**chromene-2,10-diyl) diacetate** (**1c**). Synthesized according to General Procedure A with compound **4** (0.435 g, 1.26 mmol), compound **5c** (0.588 g, 2.91 mmol), PPTS (0.035 g, 0.139 mmol), 1,2-dichloroethane (10 mL), and trimethyl orthoformate (0.57 mL, 5.2 mmol). The reaction was stirred at reflux for 2.5 h. Purification by column chromatography

on silica gel (0–15% Et_2O/CH_2Cl_2 :hexanes (1:1)) afforded the title compound (mixture of diastereomers) as a dark red oil (0.098 g, 11%).

¹<u>H NMR (400 MHz, Acetone)</u> δ: 7.69 (dd, J = 8.3, 1.2 Hz, 2H), 7.65 – 7.59 (m, 4H), 7.48 – 7.39 (m, 4H), 7.38 – 7.29 (m, 6H), 7.27 (dd, J = 8.3, 3.3 Hz, 2H), 7.07 (ddd, J = 7.5, 2.0, 1.2 Hz, 2H), 6.87 (s, 1H), 6.83 (s, 1H), 6.81 (d, J = 9.6, 1H), 6.79 (d, J = 9.6, 1H), 6.30 (d, J = 9.6 Hz, 1H), 6.27 (d, J = 9.5 Hz, 1H), 1.61 (m, 6H).

¹³C NMR (101 MHz, Acetone) δ: 170.34, 170.25, 151.0, 150.9, 147.88, 147.86, 147.6, 144.9, 144.8, 137.9, 129.0, 128.88, 128.85, 128.62, 128.57, 127.7, 127.6, 127.51, 127.46, 127.11, 127.07, 127.05, 126.22, 126.18, 125.0, 124.9, 122.37, 122.35, 121.13, 121.11, 120.1, 120.0, 118.0, 82.3, 82.2, 20.8, 20.6.

TLC (25% EtOAc/hexanes): R_f = 0.36

HRMS: calcd for $[C_{46}H_{33}O_6S]^+$ (M+H)⁺, 713.1992; found 713.2018.



2-(5-(3-(8-hydroxy-1-oxonaphthalen-2(1*H*)-ylidene)-1-phenylprop-1-en-1yl)thiophen-2-yl)-2-phenyl-2*H*-benzo[*h*]chromen-10-yl acetate (M1). Lithium diisopropylamine was freshly prepared in a flame-dried 50 mL round bottom flask. Anhydrous THF (9.5 mL) and diisopropylamine (0.145 mL, 1.035 mmol) were added via syringe under N₂. The flask was cooled to -78 °C and n-butyllithium (2.5 M in hexanes, 0.410 mL, 1.025 mmol) was added via syringe under N₂. The

reaction was stirred for 2 h. To a separate flame dried 50 mL 2-neck round bottom flask equipped with a stir bar was added **1c** (73.0 mg, 0.1025 mmol) and the vessel was evacuated and backfilled with N₂ (3x). Anhydrous THF (5 mL) was added via syringe under N₂, the solution was cooled to -78 °C, and the LDA solution (4.5 mL, 0.49 mmol) was added dropwise via syringe over the course of 8 h in 0.5–1.0 mL portions. After complete addition, the reaction was removed from the cooling bath and immediately diluted with EtOAc (50 mL) and saturated aqueous NH₄Cl solution (50 mL). The organic layer was washed with saturated aqueous NH₄Cl solution (2 x 50 mL) and then brine (50 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (0–50% EtOAc/hexanes) followed by a reverse-phase chromatographic separation on a C18 column (80–100% acetonitrile/H₂O). An additional chromatographic separation on silica gel (0–30% EtOAc/hexanes) afforded the title compound as a dark red-purple oil (0.013 g, 19%). The product is a mixture of merocyanine stereoisomers that readily interconvert (Figures S2 and S3, and Section VIII).

 $\frac{1 \text{H NMR (400 MHz, CD}_2\text{Cl}_2) \delta:}{13.67 (s, 0.08\text{H}), 13.39 (s, 0.06\text{H}), 13.29 (s, 0.52\text{H}), 8.91 (d, J = 12.4, 0.004\text{H}), 8.89 (d, J = 12.4, 0.006\text{H}), 8.74 (d, J = 12.2, 0.08\text{H}), 8.72 (d, J = 12.2, 0.02\text{H}), 8.42 (d, J = 12.1 \text{ Hz}, 0.01\text{H}), 8.10 (d, J = 12.5, 0.06\text{H}), 7.72 - 6.61 (m, 25\text{H}), 6.57 (d, J = 9.3 \text{ Hz}, 0.11\text{H}), 6.44 (d, J = 9.5 \text{ Hz}, 0.11\text{H}), 6.28 (d, J = 9.6 \text{ Hz}, 0.06\text{H}), 6.204 (d, J = 9.6, 0.21\text{H}), 6.198 (d, J = 9.6, 0.50\text{H}), 1.91 - 1.76 (m, 3\text{H}).$

¹<u>H NMR (400 MHz, THF-*d*₈) δ:</u> 13.61 (s, 0.12H), 13.50 (s, 0.01H), 13.39 (s, 0.09H), 13.30 (s, 0.59H), 8.85 (d, *J* = 12.3 Hz, 0.13H), 8.80 (d, *J* = 12.1 Hz, 0.01H), 8.54 (d, *J* = 12.3 Hz, 0.01H), 8.14 (d, *J* = 12.7 Hz, 0.07H), 7.76 – 7.71 (m, 0.13H), 7.68 – 6.67 (m, 25H), 6.57 (d, *J* = 9.4 Hz, 0.11H), 6.47 (d, *J* = 9.5 Hz, 0.12H), 6.33 (d, *J* = 9.6 Hz, 0.06H), 6.24 (d, *J* = 9.6 Hz, 0.15H), 6.22 (d, *J* = 9.6 Hz, 0.68H), 1.84 – 1.80 (m, 3H).

 $\frac{13}{2}$ NMR (101 MHz, CD₂Cl₂) δ: 189.3, 170.7, 164.8, 164.5, 152.5, 149.7, 147.3, 146.9, 144.0, 143.9, 139.7, 139.0, 137.4, 137.2, 136.6, 136.4, 131.4, 130.79, 130.77, 130.69, 130.3, 130.1, 129.7, 129.52, 129.49, 129.1, 128.80, 128.76, 128.75, 128.73, 128.62, 128.59, 128.57, 128.5, 127.6, 127.5, 127.4, 127.31, 127.29, 126.9, 126.8, 126.6, 125.8, 125.6, 125.3, 125.0, 124.8, 124.1, 123.3, 122.1, 121.4, 120.54, 120.53, 119.4, 117.43, 117.41, 116.8, 116.1, 81.8, 32.3, 30.09, 30.06, 23.1, 20.9, 14.3.

TLC (25% EtOAc/hexanes): Rf = 0.45

HRMS: calcd for $[C_{44}H_{31}O_5S]^+$ (M+H)⁺, 671.1887; found 671.1879.

N₃ OH a stir bar and reflux condenser was evacuated and backfilled with N₂ (3x). The flask was charged with anhydrous DMF (15 mL) and 8-bromooctan-1-ol (1.00 mL, 5.83 mmol) and the solution was cooled to 0 °C in an ice bath. Sodium azide (0.760 g, 11.7 mmol) was added to the reaction flask as a solid in a single portion. The reaction flask was warmed to room temperature, then heated to 80 °C and stirred for 18 h. The reaction mixture was cooled to room temperature and diluted with EtOAc (300 mL). Ice cold water (150 mL) was added, the organic layer was separated and then washed consecutively with saturated aqueous NaHCO₃ (2 x 150 mL), 10% aqueous lithium chloride (5 x 200 mL), and brine (200 mL). The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (0–50% EtOAc/hexanes) to give the title compound as a colorless liquid (0.933 g, 93%).

<u>¹H NMR (400 MHz, CDCl₃) δ</u>: 3.64 (t, *J* = 6.6 Hz, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 1.63 – 1.52 (m, 4H), 1.40 – 1.30 (m, 9H). <u>¹³C NMR (101 MHz, CDCl₃) δ</u>: 63.1, 51.6, 32.8, 29.4, 29.2, 28.9, 26.7, 25.7.

TLC (25% EtOAc/hexanes): R_f = 0.46

HRMS (ESI *m/z*): calcd for [C₈H₁₈N₃O]⁺ (M+H)⁺, 172.1450; found 172.1448.



8-Azidooctyl 2-bromo-2-methylpropanoate (Initiator). A flame-dried 50 mL twoneck round bottom flask equipped with a stir bar was evacuated and backfilled with N_2 (3x). The flask was charged with anhydrous THF (10 mL). A solution of **6** (0.870 g,

5.08 mmol) in anhydrous THF (10 mL) was added via syringe. The solution was cooled 0 °C in an ice bath, followed by the sequential addition of triethylamine (0.95 mL, 6.8 mmol) and α -bromoisobutyryl bromide (0.75 mL, 6.07 mmol). The reaction was warmed to room temperature and stirred for 24 h. The mixture was diluted with EtOAc (200 mL) and the organic layer was washed consecutively with deionized water (200 mL), saturated aqueous NaHCO₃ (2 x 200 mL), and brine (200 mL). The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (0–50% EtOAc/hexanes) to give the title compound as a colorless liquid (1.535 g, 94%).

¹<u>H NMR (400 MHz, CDCl₃) δ:</u> 4.17 (t, *J* = 6.6 Hz, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 1.93 (s, 6H), 1.72 – 1.64 (m, 2H), 1.63 – 1.55 (m, 2H), 1.44 – 1.29 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ: 171.9, 66.2, 56.1, 51.6, 30.9, 29.14, 29.12, 28.9, 28.4, 26.7, 25.8.

TLC (25% EtOAc/hexanes): R_f = 0.86

HRMS (FD m/z): calcd for $[C_{12}H_{23}BrN_3O_2]^+$ (M+H)⁺, 320.09736; found 320.09787.



General Procedure B for the Synthesis of Poly(Methyl Acrylate) (PMA) Polymers Incorporating a Terminal Azide. Polymers were synthesized by controlled radical polymerization following the procedure by Nguyen *et al.*⁵ A flame-dried Schlenk flask equipped with a stir bar was charged with freshly cut 20 G copper wire (2 cm), Initiator, DMSO, and methyl acrylate. The flask was sealed and the solution was degassed via three freeze-pump-thaw cycles, then backfilled with N₂ and warmed to room temperature. Tris[2-(dimethylamino)ethyl]amine (Me₆TREN) was added via microsyringe and the reaction was stirred at room temperature for the indicated amount of time. Upon completion of polymerization, the flask was opened to atmosphere and diluted with a minimal amount of CH₂Cl₂. The polymer was precipitated (3x) into methanol cooled with dry ice and then dried under vacuum.

PMA-Azide₂₂. Synthesized using General Procedure B with **Initiator** (57.0 mg, 0.178 mmol), methyl acrylate (4.0 mL, 44 mmol), DMSO (2.0 mL), and Me₆TREN (60 μ L, 0.22 mmol). Polymerization for 60 min provided the title polymer as a tacky colorless solid (2.4 g, 61%). M_n = 22 kg/mol, D = 1.13.

PMA-Azide. Synthesized using General Procedure B with **Initiator** (19.4 mg, 0.061 mmol), methyl acrylate (4.1 mL, 45 mmol), DMSO (4.1 mL), and Me₆TREN (33 μ L, 0.12 mmol). Polymerization for 80 min provided the title polymer as a tacky colorless solid (2.3 g, 64%). M_n = 59 kg/mol, D = 1.10.

PMA-Azide₁₉₄. Synthesized using General Procedure B with **Initiator** (3.3 mg, 0.010 mmol), methyl acrylate (2.8 mL, 31 mmol), DMSO (5.6 mL), and Me₆TREN (4.2 μ L, 0.016 mmol). Polymerization for 4 h provided the title polymer as a tacky colorless solid (1.3 g, 67%). M_n = 194 kg/mol, D = 1.09.

General Procedure C for the Synthesis of Polymers Incorporating a Chain-Centered Bis-naphthopyran. Polymers were synthesized by a Cu-catalyzed azide-alkyne cycloaddition (CuAAC) reaction based on a procedure adapted from the literature.⁶ A flame dried Schlenk flask equipped with a stir bar was charged with azide-terminated PMA polymer and pentamethyldiethylenetriamine (PMDETA). The flask was evacuated and backfilled with N₂ (3x) and brought into a glovebox. A solution of bis-alkyne functionalized bis-naphthopyran (**1a** or **1b**) in anhydrous THF was added to the flask, followed by copper(I) bromide. Additional THF was introduced to achieve a final polymer concentration of 50 mg/mL. The flask was sealed and the solution was stirred at room temperature in the glovebox for the indicated amount of time. After removal from the glovebox, the solution was filtered through a plug of basic alumina and concentrated under reduced pressure, and the residue was dissolved in a minimal amount of CH₂Cl₂. The polymer was precipitated (3x) into methanol cooled with dry ice and then dried under vacuum.



2H-BNP₄₄. Synthesized using General Procedure C with **PMA-Azide**₂₂ (0.916 g, 0.042 mmol), PMDETA (40 μ L, 0.19 mmol), **1a** (19.9 mg, 0.021 mmol), copper(I) bromide (18.0 mg, 0.125 mmol), and THF (16.4 mL) for 72 h of reaction time. The title polymer was isolated as a tacky purple solid (0.53 g, 58%). M_n = 44 kg/mol, D = 1.25.



2H-BNP₁₀₉. Synthesized using General Procedure C with **PMA-Azide** (0.980 g, 0.0166 mmol), PMDETA (16 μ L, 0.077 mmol), **1a** (7.9 mg, 0.0083 mmol), copper(I) bromide (7.1 mg, 0.050 mmol), and THF (18 mL) for 60 h of reaction time. The title polymer was isolated as a tacky pale purple solid (0.65 g, 66%). M_n = 109 kg/mol, D = 1.17.



2H-BNP₃₁₇. Synthesized using General Procedure C with **PMA-Azide**₁₉₄ (1.095 g, 0.0056 mmol), PMDETA (5.3 μ L, 0.025 mmol), **1a** (2.7 mg, 0.0028 mmol), copper(I) bromide (2.5 mg, 0.017 mmol), and THF (20 mL) for 60 h of reaction time. The title polymer was isolated as a tacky pale purple solid (0.79 g, 72%). M_n = 317 kg/mol, D = 1.17.



(9)-2*H*-BNP₁₀₄. Synthesized using General Procedure C with PMA-Azide (0.864 g, 0.0146 mmol), PMDETA (14 μ L, 0.067 mmol), **1b** (7.0 mg, 0.0073 mmol), copper(I) bromide (7.0 mg, 0.049 mmol), and THF (16 mL) for 48 h of reaction time. The title polymer was isolated as a tacky pale pink solid (0.60 g, 70%). M_n = 104 kg/mol, D = 1.13.



Figure S12. Partial ¹H NMR spectra of (a) a mixture of small molecule bis-alkyne **1a** and the mono-merocyanine species in C_6D_6 , and (b) the same solution following 1 h of irradiation with 565 nm visible light. The bis-naphthopyran **1a** is characterized by a pair of doublets at 5.76 and 5.81 ppm (J = 9.6 Hz, 2H) corresponding to pyran protons on various diastereomers. The mono-merocyanine compound is characterized by a pair of doublets at 5.84 and 5.89 ppm (J = 9.6 Hz, 2H) corresponding to pyran protons on various isomers. Before irradiation with visible light, resonances associated with the mono-merocyanine species are present, and visible light irradiation results in the significant attenuation of these peaks.

V. Characterization of PMA Polymers



Figure S13. GPC chromatograms measured with differential refractive index (dRI) and UV absorption (345 nm) detectors for **2H-BNP**₄₄ (2 mg/mL in THF, $M_n = 44$ kDa, D = 1.25), **2H-BNP**₁₀₉ (2 mg/mL in THF, $M_n = 109$ kg/mol, D = 1.17), **2H-BNP**₃₁₇ (10 mg/mL in THF, $M_n = 317$ kg/mol, D = 1.17), and **(9)-2H-BNP**₁₀₄ (2mg/mL in THF, $M_n = 104$ kg/mol, D = 1.13) overlaid with the GPC chromatograms of their respective azide-terminated poly(methyl acrylate) polymers at the same concentration.



Figure S14. Partial ¹H NMR spectra of (a) small molecule bis-alkyne **1a**, and (b) polymer **2H-BNP**₁₀₉ demonstrating successful coupling of the bis-naphthopyran unit and the polymer chains. The bis-naphthopyran at the center of polymer **2H-BNP**₁₀₉ is characterized by a pair of overlapping doublets at 6.24 and 6.25 ppm (J = 9.6 Hz, 2H) corresponding to pyran protons on various diastereomers. A new singlet (7.65 ppm, 2H) corresponds to the triazole protons generated in the CuAAC reaction. Overintegration of the overlapping signals from 7.2 to 7.5 ppm (15H versus the expected 12H) is likely due to a small amount of the merocyanine species (See section IV).



Figure S15. Partial ¹H NMR spectra of (a) small molecule bis-alkyne **1b**, and (b) polymer **(9)-2H-BNP**₁₀₄ demonstrating successful coupling of the bis-naphthopyran unit and the polymer chains. The bis-naphthopyran at the center of polymer **(9)-2H-BNP**₁₀₄ is characterized by a pair of overlapping doublets at 6.40 and 6.41 ppm (J = 9.7 Hz, 2H) corresponding to pyran protons on various diastereomers. A new singlet (7.62 ppm, 2H) corresponds to the triazole protons generated in the CuAAC reaction.

VI. DFT Calculations (CoGEF)

CoGEF calculations were performed using Spartan '20 Parallel Suite according to previously reported methods.^{7,8} Ground state energies were calculated using DFT at the B3LYP/6-31G* level of theory. Truncated models of each mechanophore with terminal acetoxy groups were used in the calculations. For each structure, the equilibrium conformations of the unconstrained molecule were initially calculated using molecular mechanics (MMFF) followed by optimization of the equilibrium geometries using DFT (B3LYP/6-31G*). Starting from the equilibrium geometry of the unconstrained molecules (energy = 0 kJ/mol), the distance between the terminal methyl groups of the truncated structures was increased in increments of 0.05 Å and the energy was minimized at each step. The maximum force associated with the mechanochemical reaction was calculated from the slope of the curve immediately prior to bond cleavage using the final two contiguous data points.



Figure S16. Density functional theory (DFT) calculations using the constrained geometries simulate external force (CoGEF) method performed on a truncated model of the 2*H*-BNP mechanophore with attachment points at the 10-position of each naphthopyran subunit. Computed structures are shown at right that correspond to the indicated points in the CoGEF profile along with the associated constraint distance between the terminal methyl groups (purple carbon atoms designate the anchor points defining the distance constraint). The first and second ring-opening reactions are predicted to occur at a maximum force of 4.2 nN and 5.0 nN, respectively. Upon further extension, an atypical ring-opening reaction is predicted to occur on both merocyanine subunits simultaneously at 5.5 nN, generating a pair of ketene and allene units as described in the main text. Calculations were performed at the B3LYP/6-31G* level of theory.

VII. Details for Photoirradiation and Sonication Experiments

Reaction progress was continuously monitored by UV-vis absorption spectroscopy using a previously described experimental setup² assembled using a peristaltic pump to transport solution from the reaction vessel through a quartz flow cell in a UV-vis spectrometer and return the solution to the reaction vessel. The flow rate through the system was maintained at 8 mL/min, corresponding to a setting of 50 RPM on the peristaltic pump at the selected occlusion. The UV-vis spectrometer was programmed to acquire full spectra at regular time intervals. Absorbance values were measured at 790 nm and subtracted from the absorbance values at all other wavelengths to account for drift during the experiments.

General Procedure for Sonication Experiments. A sonication vessel was placed onto the sonication probe and charged with anhydrous THF (18 mL) that contained 30 mM BHT to avoid decomposition side reactions resulting from free radicals generated during sonication.^{9,10} An additional 6.2 mL of stabilized THF was pumped into the

dead space of the circulatory setup. Teflon inlet and outlet tubes were inserted into the solution in the sonication vessel through punctured septa, and the pump was engaged to start the flow of solution through the system. The sonication vessel was submerged in either an ethanol bath maintained at -45 ± 2 °C with an immersion chiller or an ice bath maintained at 0 \pm 2 °C, and the solution was sparged with N₂ for 30 min. The system was then maintained under an inert atmosphere for the duration of the experiment. Continuous sonication at 20 kHz (20% amplitude, $6.8 \pm 0.5 \text{ W/cm}^2$) was initiated and run for approximately 5 min to allow the temperature inside the reaction vessel to equilibrate to -15 °C (ethanol bath) or 15-20 °C (ice bath), as measured by a thermocouple inserted into the solution (Digi-Sense EW-91428-02 thermometer with Digi-Sense probe EW-08466-83). Separately, a concentrated solution of polymer (2.0 mL, 26.2 mg/mL in stabilized THF) was sparged with N₂ for 30 min. This solution was then injected into the sonication vessel to provide a total system volume of 26.2 mL (2.0 mg/mL of polymer) and reaction progress was monitored by UV-vis absorption spectroscopy. Sonication intensity was calibrated via the literature method.¹¹ After completion of the sonication experiment, ultrasound was turned off and the temperature of the solution in the sonication vessel was allowed to equilibrate (-30 °C if the ethanol bath was used, 20 °C if an ice bath was used), after which the solution was monitored by UV-vis absorption spectroscopy for 16–20 h in the dark. The entire system was protected from external light and kept under an inert atmosphere for the duration of the experiment. A 1 mL aliquot of the sonication solution was transferred to a cuvette for bleaching experiments with visible light.

The rate of mechanochemical reactions is typically increased at lower temperatures due to the effects of decreased solvent vapor pressure on cavitation.^{12,13} Additionally, the rate of mechanochemical reactions of a chain-centered mechanophore scales with polymer chain length.¹⁴ In ultrasonication experiments of naphthopyran, low temperatures are known to slow merocyanine reversion significantly, enabling the accumulation and observation of thermally transient species.¹⁵ During the sonication of **2H-BNP**₃₁₇ at low temperatures (–15 °C), the relative rates of mechanochemical ring opening (fast) and merocyanine reversion (slow) are such that accumulation of *cis-***2H-BNP**₆₀ is observed (Figure S9).

General Procedure for Photoirradiation Experiments. Photoirradiation experiments were performed under conditions that closely mimic those of the ultrasonication experiments. A sonication vessel was placed onto the sonication probe and charged with anhydrous THF (18 mL) and an additional 6.2 mL of THF was pumped into the dead space of the circulatory setup. Teflon inlet and outlet tubes were inserted into the solution in the sonication vessel through punctured septa, and the pump was engaged to start the flow of solution through the system. The sonication vessel was lowered into an empty metal Dewar, and the solution was sparged with N₂ for 10 min. The system was then maintained under an inert atmosphere for the duration of the experiment. A solution of either polymer **2H-BNP**₁₀₉ (2 mL, 26.2 mg/mL in THF) or model compound **M1** (2 mL, 0.13 mg/mL) was sparged with N₂ for 10 minutes. This solution was then injected into the sonication vessel to provide a total system volume of 26.2 mL (2.0 mg/mL of **2H-BNP**₁₀₉ or 0.01 mg/mL of **M1**). The vessel was exposed to a UV light source (λ = 365 nm) positioned ~2 in from the vessel for the indicated amount of time, and merocyanine formation at room temperature (20 °C) was monitored by UV-vis absorption spectroscopy. Once the UV light was turned off,

absorption spectra were collected to monitor thermal reversion of the photochemically generated merocyanines. The entire system was protected from external light and kept under an inert atmosphere for the duration of the experiment. A 1 mL aliquot of the solution was transferred into a cuvette for bleaching experiments with visible light.

General Procedure for Bleaching Experiments with Visible Light. Absorption spectra of photobleached samples were measured at room temperature (20 °C) by exposing a sample solution (2.0 mg/mL of polymer in THF or 0.01 mg/mL of **M1** in THF) in a quartz cuvette to a visible light source (λ = 565 nm) positioned ~3 in from the cuvette for 30 min. The cuvette was immediately placed into the spectrometer and the absorption spectrum was collected. After a 10 min period in the dark, the cuvette was placed under the visible light source for another 30 min. This procedure was repeated until the sample had been irradiated with visible light for either 150 min or 180 min total.

VIII. Properties of H-bonded Merocyanines with Cis and Trans Exocyclic Alkenes

Naphthopyran **Mono-M1** containing a β -hydroxy ketone motif and a terminal pivalate ester exists primarily as a mixture of merocyanine species with *cis* exocyclic olefin geometry under ambient conditions (see Figure S2).¹ Irradiation with UV light promotes *cis*-to-*trans* alkene isomerization.¹⁶ To evaluate the variability in the absorption properties of the merocyanine locked with an intramolecular H-bond as a function of stereoisomer distribution, a freshly dissolved sample of **Mono-M1** in THF-*d*₈ was irradiated with UV light. Changes in the relative amount of exocyclic *cis* and exocyclic *trans* merocyanine isomers were monitored by ¹H NMR spectroscopy (600 MHz), while changes in absorption were monitored using UV-vis spectroscopy. The ¹H NMR spectrum of an unirradiated sample of **Mono-M1** contains a doublet at 8.83 ppm (*J* = 12.3 Hz) characteristic of a proton on the *cis* exocyclic alkene (H^a),¹ and a pair of overlapping doublets at 7.81 ppm (*J* = 12.8 Hz) that correspond to a proton (H^b) of the merocyanine bridge on the exocyclic *trans* isomers.¹⁶ The relative integrations of these two signals suggest that when freshly dissolved in THF-*d*₈, the exocyclic alkene of the mono-merocyanine has predominantly *cis* geometry (98%).

One drop of the above sample was diluted with non-deuterated THF and analyzed by UV-vis spectroscopy to reveal an absorption maximum at 515 nm (see Figure S2). The original sample was then irradiated with 311 nm UV light and periodically analyzed by ¹H NMR. After each NMR spectrum was collected, one drop of the NMR sample was again diluted with non-deuterated THF and analyzed by UV-vis spectroscopy. Conversion of the *cis* merocyanine is monitored by the attenuation of the doublet at 8.83 ppm (proton H^a) and concomitant generation of the *trans* merocyanine is monitored by an increase in the signals at 7.81 ppm (proton H^b). An increase in the relative amount of *trans* exocyclic alkene isomers also induces a hypsochromic shift in the absorption maximum of the merocyanine mixture (Figure S2). After 155 min of irradiation with UV light, the ¹H NMR spectrum suggests that only 31% of the merocyanine species have *cis* geometry of the exocyclic olefin, while 69% of merocyanines have *trans* geometry. This change in alkene isomerism corresponds to a shift in the absorption maximum from 515 to 500 nm. To evaluate the impact of *cis* and *trans* isomerism of the exocyclic alkene on the observed extinction coefficient at a given wavelength, a ~10 μ M solution of **Mono-M1** in THF was prepared and transferred to a sealed cuvette (see Figure S3). The sample was irradiated with 311 nm UV light and analyzed by UV-vis absorption spectroscopy. Using the quantitative ¹H NMR data described in Figure S2, a linear relationship between *cis* exocyclic alkene content and absorption maximum was determined (Figure S2*c*, inset). Using this relationship, the relative ratio of merocyanine isomers with *cis* and *trans* exocyclic alkenes was determined based on the absorption maximum of the mixture. The mixture was converted from 89% to 41% *cis* geometry after exposure to UV light for 420 s. Concurrently, the absorbance at λ_{max} of the sample increased by approximately 7%, from 0.197 to 0.211. The data presented in Figures S2 and S3 indicate that merocyanine isomers containing a single intramolecular H-bond and a *cis* exocyclic alkene have a smaller extinction coefficient and exhibit a bathochromically shifted absorption maximum compared to the *trans* isomer. Notably, *cis*-to-*trans* isomerization of **Mono-M1** is also observed in the dark in the presence of small amounts of water (Figure S17).



Figure S17. UV-vis absorption spectra of **Mono-M1** in THF (10 μ M) illustrating *cis*-to-*trans* isomerization of the exocyclic alkene in the presence of a small amount of water. (a) Minimal change is observed in the absorption spectrum of a freshly prepared solution of **Mono-M1** after storage for 3 days at 20 °C in the dark. (b) The absorption spectrum of a solution of **Mono-M1** containing 4.3% water (by volume) changes significantly over a period of six days. A hypsochromic shift of λ_{max} is accompanied by an increase in absorbance. These spectral changes correspond to a change in the distribution of merocyanine isomers from 98% to 32% *cis*.

The ¹H NMR spectra of **2H-BNP**₁₀₉ before and after ultrasonication are illustrated in Figure S18, along with the ¹H NMR spectrum of model compound **M1**. The bis-naphthopyran unit in polymer **2H-BNP**₁₀₉ is characterized by a pair of overlapping doublets at 6.14 and 6.15 ppm (J = 9.6 Hz) corresponding to pyran protons on various diastereomers. The pyran ring in model compound **M1** is characterized by a doublet at 6.22 ppm (J = 9.6 Hz).

Signals attributed to the OH proton of various merocyanine isomers appear in the 13.0–14.0 ppm region in the spectra of **M1** and **2H-BNP**₁₀₉ after mechanochemical activation. Photoisomerization of **Mono-M1** (see Figure S2) suggests that the singlet at 13.30 ppm belongs to H-bonded merocyanine isomers with *trans* configuration of the exocyclic olefin, and the singlets at 13.62 and 13.64 ppm belong to *cis* isomers. The minor sets of doublets at 8.86 and 8.94 ppm (J = 12.3 and J = 12.4 Hz, respectively) are attributed to protons on various isomers of the H-bonded merocyanine subunit with *cis* configuration of the exocyclic alkene and account for approximately 32% of the total H-bonded merocyanine present in the sample of **2H-BNP**₁₀₉ after ultrasonication. We note that this does not necessarily reflect the actual product distribution from the mechanochemical reaction due to the spontaneous *cis*-to-*trans* isomerization that is observed in the presence of water (see Figure S17).



Figure S18. Partial ¹H NMR spectra of (a) **2H-BNP**₁₀₉, (b) model compound **M1**, and (c) **2H-BNP**₁₀₉ after mechanochemical activation (12 h of continuous ultrasonication, 30 mM BHT in THF, 20 °C).

IX. References

- (1) McFadden, M. E.; Robb, M. J. Generation of an Elusive Permanent Merocyanine via a Unique Mechanochemical Reaction Pathway. *J. Am. Chem. Soc.* **2021**, *143*, 7925–7929.
- (2) McFadden, M. E.; Robb, M. J. Force-Dependent Multicolor Mechanochromism from a Single Mechanophore. *J. Am. Chem. Soc.* **2019**, *141*, 11388–11392.
- (3) Zhao, W.; Carreira, E. M. Facile One-Pot Synthesis of Photochromic Pyrans. Org. Lett. 2003, 5, 4153–4154.
- (4) Zhao, W.; Carreira, E. M. Oligothiophene-Linked Bisnaphthopyrans: Sequential and Temperature-Dependent Photochromism. *Chem. Eur. J.* **2007**, *13*, 2671–2685.
- (5) Nguyen, N. H.; Rosen, B. M.; Lligadas, G.; Percec, V. Surface-Dependent Kinetics of Cu(0)-Wire-Catalyzed Single-Electron Transfer Living Radical Polymerization of Methyl Acrylate in DMSO at 25 °C. *Macromolecules* **2009**, *42*, 2379–2386.
- (6) Nixon, R.; De Bo, G. Three concomitant C–C dissociation pathways during the mechanical activation of an Nheterocyclic carbene precursor. *Nat. Chem.* **2020**, *12*, 826–831.
- (7) Beyer, M. K. The mechanical strength of a covalent bond calculated by density functional theory. *J. Chem. Phys.* **2000**, *112*, 7307–7312.
- (8) Klein, I. M.; Husic, C. C.; Kovács, D. P.; Choquette, N. J.; Robb, M. J. Validation of the CoGEF Method as a Predictive Tool for Polymer Mechanochemistry. *J. Am. Chem. Soc.* **2020**, *142*, 16364–16381.
- (9) Yang, J.; Horst, M.; Werby, S. H.; Cegelski, L.; Burns, N. Z.; Xia, Y. Bicyclohexene- *peri* -naphthalenes: Scalable Synthesis, Diverse Functionalization, Efficient Polymerization, and Facile Mechanoactivation of Their Polymers. *J. Am. Chem. Soc.* **2020**, *142*, 14619–14626.
- (10) Overholts, A. C.; McFadden, M. E.; Robb, M. J. Quantifying Activation Rates of Scissile Mechanophores and the Influence of Dispersity. *Macromolecules* **2022**, *55*, 276–283.
- (11) Berkowski, K. L.; Potisek, S. L.; Hickenboth, C. R.; Moore, J. S. Ultrasound-Induced Site-Specific Cleavage of Azo-Functionalized Poly(ethylene glycol). *Macromolecules* **2005**, *38*, 8975–8978.
- (12) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Mechanically-Induced Chemical Changes in Polymeric Materials. *Chem. Rev.* **2009**, *109*, 5755–5798.
- (13) May, P. A.; Moore, J. S. Polymer mechanochemistry: techniques to generate molecular force via elongational flows. *Chem. Soc. Rev.* **2013**, *42*, 7497–7506.
- (14) May, P. A.; Munaretto, N. F.; Hamoy, M. B.; Robb, M. J.; Moore, J. S. Is Molecular Weight or Degree of Polymerization a Better Descriptor of Ultrasound-Induced Mechanochemical Transduction? *ACS Macro Lett.* 2016, *5*, 177–180.
- (15) Osler, S. K.; McFadden, M. E.; Robb, M. J. Comparison of the reactivity of isomeric 2H- and 3H-naphthopyran mechanophores. *J. Polym. Sci.* **2021**, *59*, 2537–2544.
- (16) Aiken, S.; Booth, K.; Gabbutt, C. D.; Heron, B. M.; Rice, C. R.; Charaf-Eddin, A.; Jacquemin, D. The first structural and spectroscopic characterisation of a ring-opened form of a 2H-naphtho[1,2-b]pyran: a novel photomerocyanine. *Chem. Commun.* **2014**, *50*, 7900.





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