# Electronic Supplementary Information (ESI)

# Cyclic Cinnamate Dimer Mechanophore for Multimodal Stress-Responsive and Mechanically Adaptable Polymeric Materials

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# Synthesis

# Materials, NMR and GPC

5-dibenzosuberenone, benzophenone, citric acid, ethylene glycol, potassium perchlorate were purchased from Energy. Maleic anhydride, 1,5-pent- anedioic acid, 4-dimethylaminepyridine, N,N'-methane-tetraylbis(1-methylethylamine), were obtained from Alladin. Dichloromethane were distilled over  $CaH_2$  under nitrogen. All other reagents were purchased from Sinopharm and used without further purification.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sup>3</sup> ( $\delta$ = 7.26 (<sup>1</sup>H) and 77.16 (<sup>13</sup>C)) and referenced to the residual solvent signals on a 500 MHz Brucker AvanceII spectrometer at 25 °C. All chemical shifts were given in ppm ( $\delta$ ) as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), or broad (br).

Gel permeation chromatography (GPC) data were calibrated on two in series columns (7.8  $\times$  300 mm, 2 GMHHRM17932 and 1 GMHHRH17360) with tetrahydrofuran (THF, HPLC grade) as eluent at 40 °C with a LC-20AD pump. The facility was equipped with two detectors (RID-10A refractive index detector; SPD-20A UV detector) and the molecular weight was calibrated against polystyrene standards.

# Synthesis of the non-scissile cinnamic acid dimer mechanophore

# Synthesis of compound 1<sup>[1]</sup>

# (1R,2S)-7-oxo-2,2a,7,11b-tetrahydro-1H-dibenzo[a,e]cyclobuta[c][7]annulene-1,2dicarboxylic acid

A solution of 5-dibenzosuberenone (2.0 g, 9.7 mmol, 1 equiv.), maleic anhydride (9.5 g, 97 mmol, 10 equiv.) in toluene (400 mL) and 1,4-dioxan (67 mL) placed in a cylindrical watercooled reactor was degassed with an nitrogen stream for 30 min, then sealed. The solution was then irradiated for 48 h with a 400 W medium-pressure mercury lamp fitted with a Pyrex filter. The solution was then evaporated under reduced pressure and ten residue was dissolved in THF (160 mL) and 2N NaOH (122 mL) was added. The mixture was stirred at room temperature for 2.5 hours. The THF was removed and remaining aqueous was extracted with EtOAc for five times. The aqueous was acidified to ca. pH 3 with solid citric acid and extracted with EtOAc for five times. The second EtOAc extraction was dried with anhydrous MgSO<sub>4</sub> and evaporated under reduced pressure to give compound **1** as yellow powder in 76% yield. <sup>1</sup>H NMR (500 MHz, CDCl3)  $\delta$  (ppm) 12.55 (br, 2H), 7.54 (m, 4H), 7.39 (t, *J* = 7.39 Hz, 2H), 7.31 (d, *J* = 7.39 Hz, 2H), 4.36 (d, *J* = 6.03 Hz, 2H), 3.22 (d, *J* = 7.39 Hz, 2H). <sup>13</sup>C NMR (500 MHz, DMSO)  $\delta$  (ppm) 200.48, 173.20, 140.48, 138.95, 133.02, 130.62, 128.95, 128.05, 48.00, 43.78. Esquire 3000 Plus - ESI (*m*/*z*): calcd for C<sub>19</sub>H<sub>14</sub>O<sub>5</sub> [M Na<sup>+</sup>] 345.31, [M H<sup>+</sup>] 323.09; found, 344.8, 322.8.

# Synthesis of chloridized 1 (1R,2S)-7-oxo-2,2a,7,11b-tetrahydro-1H-dibenzo[a,e]cyclobuta[c][7]annulene-1,2dicarbonyl dichloride

Thionyl chloride (SOCl<sub>2</sub>) (1.8 mL, 24.8 mmol, 4 equiv.) and two drops of dimethylformamide (DMF) were added to a stirred solution of compound 1 (2.0 g, 6.2 mmol, 1 equiv.) in dry chloroform (CHCl<sub>3</sub>) (30 mL). The mixture was refluxed for 12 h and allowed to cool to room temperature. The solvent and the unreacted SOCl<sub>2</sub> were removed under vacuum. The acid chloride derivative was directly used in the next step. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm)

7.69 (d, *J* = 7.57 Hz, 2H), 7.53 (t, *J* = 7.31 Hz, 2H), 7.42 (t, *J* = 7.57 Hz, 2H), 7.34 (d, *J* = 7.46 Hz, 2H), 4.45 (d, *J* = 5.51 Hz, 2H), 3.88 (d, *J* = 5.51 Hz, 2H).

# Synthesis of compound 2

# bis(2-hydroxyethyl)(1R,2S)-7-oxo-2,2a,7,11b-tetrahydro-1H-dibenzo[a,e]cyclobuta[c][7] annulene-1,2-dicarboxylate

A solution of chloridized compound **1** (2.2g, 6.2 mmol, 1equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added dropwise to a stirred solution of ethylene glycol (13.8 mL, 0.25 mol, 40 equiv.) and triethylamine (TEA) (1.72 mL, 12.4 mmol, 2 equiv.) in dry dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (10 mL). The reaction mixture was stirred at room temperature overnight. The organic layer was then washed sequentially with 1 M chlorydric acid (HCl) (50 mL), 10% sodium hydrogenocarbonate (NaHCO<sub>3</sub>) (50 mL) and saturated brine (50 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was further evaporated under vacuum to give a crude product which was purified with column chromatography (hexane/ethyl acetate = 1:6) to give compound **2** ( yield 77%) as an yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl3)  $\delta$  (ppm) 7.66 (d, *J* = 7.71 Hz, 2H), 7.46 (t, *J* = 7.58 Hz, 2H), 7.35 (t, *J* = 7.56 Hz, 2H), 7.24 (t, *J* = 7.57 Hz, 2H), 4.50 (d, *J* = 6.34 Hz, 2H), 4.34 (m, 2H), 4.17 (m, 2H), 3.81 (s, 4H), 3.51 (d, *J* = 6.33 Hz, 2H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 200.58, 172.07, 140.41, 137.9, 132.63, 130.17, 129.34, 127.96, 66.98, 60.71, 48.06, 44.37. Esquire 3000 Plus - ESI (*m*/*z*): calcd for C<sub>23</sub>H<sub>22</sub>O<sub>7</sub> [M Na<sup>+</sup>] 433.41; found, 432.9.

#### **Polymer synthesis**

#### Synthesis of polyester P2 and P2C

Compound **2** (0.513 g, 1.25 mmol, 1 equiv.), glutaric acid (0.1653 g, 1.25 mmol, 1 equiv.), and dimethylaminopyridinium toluenesulfonate (0.147 g, 0.5 mmol, 0.4 equiv.) were added to a 25 mL flask. Dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added by syringe, and the solution was heated to 37°C while stirring until solution became homogenous. After cooling to room temperature, N,N-diisopropylcarbodiimide (0.58 mL, 3.75 mmol, 3 equiv.) was added dropwise by syringe. The mixture was stirred for 96 h. The mixture was precipitated twice from CH<sub>2</sub>Cl<sub>2</sub> into MeOH to afford a white solid **P2**. <sup>1</sup>H NMR (500 MHz, CDCl3)  $\delta$  (ppm) 7.62 (d, *J* = 7.17 Hz, 2H), 7.44 (t, *J* = 6.98 Hz, 2H), 7.66 (d, *J* = 7.37 Hz, 2H), 7.22 (d, *J* = 7.30 Hz, 2H), 4.42 (m, 2H), 4.32 (m, 2H), 4.22 (m, 6H), 3.43 (d, *J* = 3.74 Hz, 2H), 2.37 (t, *J* = 6.93 Hz, 4H), 1.91 (t, *J* = 6.65 Hz, 2H).

#### Synthesis of polyester P2C

Compound **2** (0.513 g, 1.25 mmol, 1 equiv.), glutaric acid (0.1653 g, 1.25 mmol, 1 equiv.), and dimethylaminopyridinium toluenesulfonate (0.147 g, 0.5 mmol, 0.4 equiv.) were added to a 25 mL flask. Dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added by syringe, and the solution was heated to 37°C while stirring until solution became homogenous. After cooling to room temperature, N,N-diisopropylcarbodiimide (0.58 mL, 3.75 mmol, 3 equiv.) was added dropwise by syringe. The mixture was stirred for 24 h. The mixture was precipitated twice from CH<sub>2</sub>Cl<sub>2</sub> into MeOH to afford a white solid **P2C**. <sup>1</sup>H NMR (500 MHz, CDCl3)  $\delta$  (ppm) 7.62 (d, *J* = 7.17 Hz, 2H), 7.44 (t, *J* = 6.98 Hz, 2H), 7.66 (d, *J* = 7.37 Hz, 2H), 7.22 (d, *J* = 7.30 Hz, 2H), 4.42 (m, 2H), 4.32 (m, 2H), 4.22 (m, 6H), 3.43 (d, *J* = 3.74 Hz, 2H), 2.37 (t, *J* = 6.93 Hz, 4H), 1.91 (t, *J* = 6.65 Hz, 2H).

#### **Ultrasound Sonication**

Ultrasound experiments were performed on a Vibra Cell 505 liquid processor with a 12.8 mm (diameter) titanium solid probe (Sonics and Materials). For typical sonication experiment, polymers were dissolved in THF with a concentration of 5 mg/mL in 19 mL of solvent. The solution was then transferred to a 3-necked Suslick cell in an ice bath and sparged with nitrogen for 30 min. A pulse sequence of 1s on/1s off was applied to the solution at a power of 8.7 W/cm<sup>2</sup>. The temperature of the system was maintained at  $-5 - 0^{\circ}$ C. The sonication was carried out under a nitrogen atmosphere.

Aliquots (0.8 mL, 5 mg/mL) at given time were removed from the Suslick cell for GPC and UV-Vis test. After sonication, the residual solution was precipitated by methanol and redissolved in  $CDCl_3$  (~ 25 mg/mL) for <sup>1</sup>H NMR measurement.

#### Healing of bisected P2 film

A light yellow strip (2.53 mm wide and 0.31 mm thick) was bisected by a razor blade and the two halves were brought in contact. Solvent (dichloromethane) was dropped in the contact region and the wound was irradiated under UV light for 4 h (365 nm, 1.68 W cm-2) while the rest part was masked from UV light.

# **Film preparation**

Films of intact **P2** were cast from  $CH_2Cl_2$  solution (40 mg/mL). Films of sonicated **P2** were cast from a solution obtained by concentrating a THF solution of **P2** that was sonicated for 4 h as described in the preceding section. Films of sonicated and UV irradiated material (denoted as healed/sonic **P2**) were obtained by irradiating films of sonicated **P2** at 365 nm (1.68 W cm<sup>-2</sup>) for 4 hours. All films were 0.3 mm thick and cut into rectangular strips (8.0 × 1.3 × 0.3 mm) for tensile testing.

# **Mechanical experiments**

Measurements were performed on an Instron 3343 tensile tester. Strips were directly mounted on the grips and the initial strain rate was 0.02 s<sup>-1</sup>. Mechanical data are presented as nominal stress =  $F/S_0$  (*F* is the force at the grips and  $S_0$  is the area of the cross section before deformation) as a function nominal strain =  $\Delta L/L_0$ , where  $\Delta L$  and  $L_0$  are the extension and the original length of the strip, respectively.

# Quantum chemical calculation

All the quantum chemical calculations have been carried out by Gaussian 09 program at the B3LYP/6-31 + G\* level. The CoGEF (constrained geometry simulates external force) method<sup>[2]</sup> is employed to calculate the force-induced length changes. Briefly, the distance between the two O atoms (see **Supporting Figure 9**) was incremented in steps of 0.025 Å. Then the constrained geometry optimization is performed with this distance between the two O atoms kept constant. The CoGEF plots of energy vs. the distance were then fitted by a quadratic fit to generate a function of energy vs. distance. A derivative of the energy-distance

function gave force as a function of distance. *Extrapolation of the force – distance plot to the zero forces yielded the contour length*.<sup>[3-6]</sup>

For simplicity, we choose model analogues to compound 2 and 3 (Entry 1 - 7 in **Table S3**) for quantum chemical calculations. For compound 2, <sup>1</sup>H NMR and <sup>13</sup>C NMR revealed two types of H atoms and C atoms around the cyclobutane core (**Supporting Figure 1**), suggesting two possible stereo structures of compound 2 (Entry 1 and 2). The free energy of Entry 1 is 6.47 kcal/mol smaller than that of Entry 2, hence the former one is more stable than the latter. Entry 3 and Entry 4 are two other diastereomers for comparison. For compound 3, <sup>1</sup>H NMR showed both *trans*- and *cis*-cinnamates. We therefore calculated all possible combinations: *E*,*E*-diene (Entry 5), *E*,*Z*-diene (Entry 6), and *Z*, *Z*-diene (Entry 7).



Supporting Figure 1. NMR spectra of compound 1. (a) <sup>1</sup>H NMR; (b) <sup>13</sup>C NMR



**Supporting Figure 2.** <sup>1</sup>H NMR spectra of chloridized **1**.





**Supporting Figure 4.** Spectroscopic characterization of **P2** and **P2C**. (a) <sup>1</sup>H NMR; (b) GPC trace (RI) of **P2**; (c) GPC trace (RI) of **P2C**.



**Supporting Figure 5.** <sup>1</sup>H NMR spectra of **P2** before (black) and after (red) 18 h heating in DMSO-d at 150 °C.



**Supporting Figure 6.** <sup>1</sup>H NMR spectra of small molecule **2** before (black) and after (red) 18 h heating in DMSO-d at 150 °C.



**Supporting Figure 7.** Refractive index of a control polymer **PC2** (5 mg mL<sup>-1</sup>) after sonication. Numbers in the legend indicate the sonication time.



**Supporting Figure 8.** <sup>1</sup>H NMR spectra of a control polymer **PC2** (5 mg mL<sup>-1</sup>) before (black) and after (red) sonication. Numbers in the legend indicate the sonication time.



**Supporting Figure 9.** Quadratic fit of energy vs. distance (O-O, marked by double-headed arrows) and force-distance vs. distance for analogues of compound **2** and moiety **3**. (a-b) dimethyl

(1R,2S,2aR,11bS)-7-oxo-2,2a,7,11b-tetrahydro-1H-dibenzo[a,e]cyclobuta[c][7]annulene-1,2-dicarboxylate. (c-d) dimethyl 3,3'-(carbonylbis(2,1-phenylene))(2E,2'E)-diacrylate. (e-f) methyl (Z)-3-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)benzoyl)phenyl)acrylate. (g-h) dimethyl 3,3'-(carbonylbis(2,1-phenylene))(2Z,2'Z)-diacrylate. All calculation are based on B3LYP/6-31 + G\* level DFT.



Supporting Figure 10. Stress-strain curves of pristine P2, UV-irradiated P2 (for 4 h), sonicated P2, and sonicated and healed P2 films.



**Supporting Figure 11.** Proposed mechanism of on-demand strengthening/healing by UV light for P2 in which the MTCD moieties are unactivated (by mechanical force)



**Supporting Figure 12.** Refractive index traces of **P2** (5 mg mL<sup>-1</sup>) at difference sonication time indicated in the legend.



Supporting Figure 13. Weight-average molecular weight  $M_w$  of P2 (5 mg mL<sup>-1</sup>) as a function of sonication time.

Ultrasonication often causes random-chain-fragmentation of polymers. In our case, the weightaveraged molecular weight of **P2** reduced to halve of its original value after 4 h sonication.



**Supporting Figure 14.** Proposed strengthening/healing mechanisms in sonicated **P2** by UV light. Generation of diradicals in **2** (a) and **3** (b) under UV light. (c) Possible new load-bearing bonds (red) via radical recombination between neighboring macroradicals.



**Supporting Figure 15.** The small molecule precusor **1** reacts with TEMPO under UV irradical revealed by <sup>1</sup>H NMR.

*Table S1* Molecular parameters of **P2** and **P2C**.

Entry	M <sub>n</sub> (KDa)	$M_{ m w}$ (KDa)	PDI
P2	24	32	1.35
P2C	3.7	4.9	1.31

Table S2 Summarization of quantum chemical calculations.

Entry	Chemical structure	Optimized Geometry <sup>a</sup>	Energy (a.u.) <sup>a</sup>	d (O-O) (Å) <sup>b</sup>
1			-1187.225058	4.99
2			-1187.214752	5.45
3			-1187.229449	4.03
4			-1187.229773	4.14
5		مرون مرون مورد مرون مرون مرون مرون مرون مرون مرون مرون مرون	-1187.229025	11.6
6			-1187.209331	12.3



<sup>a</sup> Calculated at force-free state

<sup>b</sup> Calculated by extroplation of the force – distance plots to the zero force.

Sonication time/h	$M_{\rm w}$ (KDa)	$M_{\rm n}({\rm KDa})$	PDI
0	32.5	24.1	1.35
0.17	31.0	23.9	1.30
0.5	27.8	22.0	1.27
1	25.8	21.1	1.23
2	22.5	19.1	1.18
3	20.7	17.7	1.17
6	16.8	14.8	1.14

*Table S3* Change of molecular weight and polydispersity of **P2** during ultrasonication.

Table S4 Summary of mechanical data.

Trial	Modulus (MPa)			Ultimate strength (MPa)				
	P2	UV-	Sonic. P2	Healed	P2	UV-	Sonic.	Healed
		treated		/sonic.		treated	P2	/sonic.
		P2		P2		P2		P2
1	123	210	2.8	114	3.5	7.9	0.05	3.6
2	51	249	3.9	79	3.5	7.0	0.14	2.3
3	181	247	2.3	146	5.1	7.5	0.12	4.6
average	118	236	3.0	113	4.0	7.5	0.11	3.5
Std dev.	65	22	0.8	34	0.9	0.4	0.04	1.2

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