Supporting information for

Interfacial Mechanophore Activation
Using Laser-Induced Stress Waves

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1. General Experimental Details

Reagents from commercial sources were used without further purification unless otherwise stated. Dry THF was obtained from a solvent purification system equipped with activated alumina columns and stored over 3Å molecular sieves. All reactions were performed under a N_2 atmosphere unless specified otherwise. Column chromatography was performed on a Biotage Isolera system using SiliCycle SiliaSep HP flash cartridges. NMR spectra were recorded using a Varian 500 MHz spectrometer. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in deuterated solvent. All ^{13}C NMR spectra were measured in deuterated solvents and are reported in ppm relative to the signals for residual chloroform (77.16 ppm). Mass spectra were obtained through the Mass Spectrometry Laboratory, School of Chemical Sciences, at the University of Illinois.

2. Mechanophore Synthesis
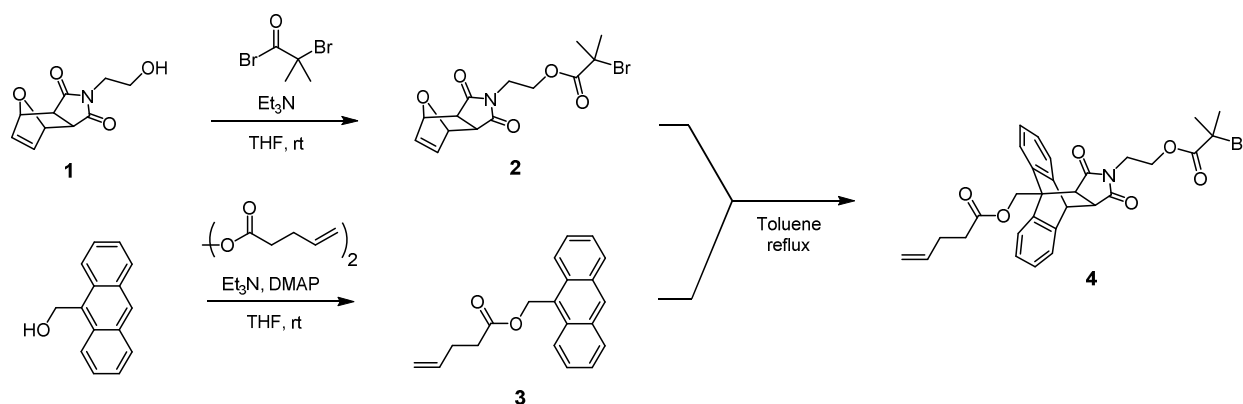
4-(2-bromoisobutyroxy)ethyl-10-oxa-4-aza-tricyclo[5.2.1.0^{2,6}]-dec-8-ene-3,5-dione (2). An oven-dried 50 mL round bottom flask equipped with a stir bar was charged with **1**[1] (2.0 g, 9.6

mmol) and dry THF (20 mL) and sealed with a septum. Triethylamine (1.5 mL, 11 mmol) was added via syringe followed by the dropwise addition of α-bromoisobutyryl bromide (1.3 mL, 11 mmol). After stirring at room temperature for several days, the reaction mixture was filtered through a pad of silica gel, washing thoroughly with ethyl acetate. The filtrate was concentrated under reduced pressure to provide the title compound as a slightly yellow oil (3.5 g, quant). ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.89 (s, 6H), 2.86 (s, 2H), 3.81 (t, J=5.2 Hz, 2H), 4.32 (t, J=5.2 Hz, 2H), 5.26 (s, 2H), 6.51 (s, 2H) ppm. ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$) δ: 30.7, 37.7, 47.6, 55.8, 62.3, 81.0, 136.7, 171.5, 176.0 ppm. HRMS (ESI, m/z): calcd for [C$_{14}$H$_{17}$BrNO$_5$]$^+$ (M+H)$^+$, 358.0285; found, 358.0287.

Anthracen-9-ylmethyl pent-4-enoate (3). A 50 mL round bottom flask equipped with a stir bar was charged with 9-anthracenemethanol **(**1.9 g, 9.1 mmol), DMAP (0.14 g, 1.1 mmol), and THF (23 mL) and sealed with a septum. Triethylamine (1.6 mL, 11 mmol) was added via syringe followed by 4-pentenoic anhydride (2.0 mL, 11 mmol). After stirring at room temperature overnight, the reaction mixture was diluted with ethyl acetate and washed consecutively with 10% NaHSO$_4$ (50 mL), 10% NaHCO$_3$ (50 mL), and brine (50 mL), dried over MgSO$_4$, filtered, and concentrated under reduced pressure to provide the title compound as a yellow liquid (2.7 g, quant). ^{1}H NMR (500 MHz, CDCl$_3$) δ: 2.35–2.47 (m, 4H), 4.94–5.04 (m, 2H), 5.79 (ddt, J=16.6, 10.2, 6.2 Hz, 1H), 6.16 (s, 2H), 7.50 (ddd, J=7.8, 6.5, 1.0 Hz, 2H), 7.58 (ddd, J=8.8, 6.6, 1.4 Hz, 2H), 8.01–8.07 (m, 2H), 8.33 (dd, J=8.8, 1.1 Hz, 2H), 8.52 (s, 1H) ppm. ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$) δ: 29.0, 33.7, 58.9, 115.7, 124.1, 125.2, 126.3, 126.7, 129.2, 129.3, 131.1, 131.5, 136.7, 173.4 ppm. HRMS (EI, m/z): calcd for [C$_{20}$H$_{18}$O$_2$]$^+$ (M)$^+$, 290.1301; found, 290.1306.

Diels-Alder adduct (4). A 50 mL round bottom flask equipped with a stir bar and reflux condenser was charged with **2** (1.8 g, 5.0 mmol), **3** (1.5 g, 5.2 mmol), and toluene (20 mL). After refluxing for 19 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by column chromatography (5–30% EtOAC/hexanes) to provide **4** as a white solid (2.4 g, 83%). ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.88 (s, 6H), 2.43–2.49 (m, 2H), 2.53–2.58 (m, 2H), 3.27–3.41 (m, 4H), 3.59–3.71 (m, 2H), 4.78 (d, J=2.9 Hz, 1H), 5.02–5.12 (m, 2H), 5.42–5.54 (m, 2H), 5.86 (ddt, J=16.7, 10.2, 6.3 Hz, 1H), 7.15–7.22 (m, 5H), 7.28–7.33 (m, 2H), 7.38–7.43 (m, 1H) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 29.0, 30.7, 30.8, 33.7, 36.8, 45.7, 45.8, 47.8, 55.7, 61.7, 62.2, 115.9, 122.2, 123.2, 124.3, 125.4, 126.8, 127.0, 127.3, 127.3, 136.6, 138.2, 138.7, 141.2, 141.9, 171.3, 172.9, 175.1, 176.2 ppm. HRMS (ESI, m/z): calcd for $[C_{30}H_{31}BrNO_6]^+$ (M+H)$^+$, 580.1329; found, 580.1341.
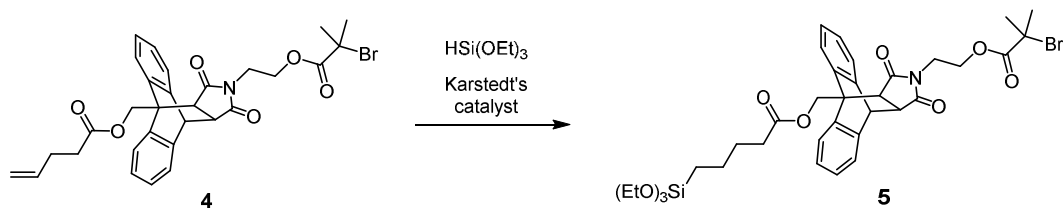
Triethoxysilyl functionalized Diels-Alder adduct (5). An oven-dried 10 mL Schlenk flask equipped with a stir bar was charged with **4** (0.85 g, 1.5 mmol) and sealed with a septum. The flask was evacuated and backfilled with nitrogen (3x) followed by the addition of triethoxysilane (2.7 mL, 15 mmol) and Karstedt's catalyst (5 µL, 2% Pt in xylene) via syringe. After stirring overnight at room temperature, the reaction mixture was concentrated under reduced pressure to afford the crude product as a clear viscous oil, which was used without further purification (0.98 g, 88% conversion by ^{1}H NMR). ^{1}H NMR (500 MHz, CDCl$_3$) δ: 0.60–0.68 (m, 2H), 1.21 (t, J=7.0 Hz, 7H), 1.45–1.54 (m, 2H), 1.70–1.79 (m, 2H), 1.88 (s, 6H), 2.41–2.48 (m, 2H), 3.28–

3.42 (m, 4H), 3.59–3.70 (m, 2H), 3.80 (q, J=7.0 Hz, 5H), 4.78 (d, J=2.5 Hz, 1H), 5.40–5.54 (m, 2H), 7.15–7.24 (m, 5H), 7.27–7.32 (m, 2H), 7.38–7.42 (m, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl$_3$) δ: 10.3, 18.5, 22.7, 28.5, 30.8, 34.2, 36.8, 45.8, 47.9, 55.7, 58.5, 61.6, 62.2, 122.3, 123.2, 124.3, 125.5, 126.9, 127.0, 127.3, 127.4, 138.3, 138.7, 141.2, 141.9, 171.4, 173.6, 175.2, 176.3 ppm. HRMS (ESI, m/z): calcd for $[C_{36}H_{46}BrNNaO_9Si]^+$ (M+Na)$^+$, 766.2017; found, 766.2023.

3. Sample Fabrication Process

3.1 Control specimen preparation

Fused silica substrates (1.5 mm thick, GM associates) were cleaned in piranha solution at 120 °C for 30 minutes. Cleaned substrates were washed with DI water and dried in a stream of air. The substrates were further dried in a convection oven at 120 °C for 30 min. For surface functionalization, cleaned substrates were immersed in a 10 mM toluene solution of functionalized maleimide-anthracene **5** and kept in a sealed container for 24h on a benchtop. After 24h, the substrates were sonicated in toluene and subsequently rinsed with toluene, isopropyl alcohol, and DI water followed by drying under a stream of air.

3.2 Active specimen preparation

3.2.1 Azide-terminated maleimide-anthracene specimens

Active specimens contained an amine-functionalized maleimide-anthracene mechanophore anchored to the silica surface. First, specimens containing an azide-functionalized mechanophore surface were prepared by conversion of the bromine-terminated specimens above following a procedure described previously.[2] Substrates were immersed in a saturated solution of sodium

azide in anhydrous-DMF for 24h at room temperature. After 24h, the substrates were rinsed with DMF, sonicated in ethanol for 3 minutes, rinsed with DI water, and dried in a stream of air. Reaction was confirmed using XPS (Figure S3).

3.2.2 Amine-terminated maleimide-anthracene specimens

Amine-terminated samples were prepared by conversion of the azide-terminal group to an amine group through Staudinger reaction.[3] Azide-terminated substrates were immersed in a 13 mM THF solution of triphenylphosphine (1 equiv.) for 12 h. After 12h, DI water (10 equiv) was added to the solution and kept for 12h at room temperature. When the reaction was completed, the substrates were rinsed in THF, ethanol, and DI water. Reaction was confirmed using XPS (Figure S3).

3.3 Patterning epoxy film on substrate

Photopatternable epoxy was synthesized using a method reported previously.[4] 10 g Epon 1002-F (Hexion), 1.25 g triarylsulfonium hexafluoroantimonate salts (Sigma-Aldrich), 15 g Gamma-butyrolactone was used as the photoresist resin. 3 droplets of the epoxy resin was spin-coated at 3000 rpm for 45 seconds on a functionalized substrate. Residual solvent was evaporated at 110°C for 2 minutes. The spin-coated resin was then exposed to 200 mJ/cm^2 of UV source under iron oxide photomask and baked for 5 minutes at 100°C. After baking, the photoresist was developed using SU-8 developer. The epoxy was further hard baked at 120°C for 30 minutes to ensure full crosslinking and covalent bonding with the amine functional group of the maleimide-anthracene adduct. The resulting epoxy film was measured to be 1.5 μm thick with a profilometer.

3.4 Deposition of aluminum absorption film and sodium silicate confining layer

After patterning the epoxy thin film, a 400 nm thick aluminum absorbing layer was deposited by e-beam evaporation (Temescal E-Beam Evaporation Systems) on the back side of the specimen. A 1 μm thick sodium silicate (Fisher Scientific) confining layer was deposited by spin coating a sodium silicate solution on top of Al at 3000 rpm for 45 seconds.

4. Fluorescence Images

Fluorescence images were acquired using a Zeiss Axiovert 200M with Cascade 512b high sensitivity camera. A mercury lamp source was used with 360 nm centered/FWHM 11 nm band pass excitation filter, 410 nm pass dichroic mirror, and 420 nm/FWHM 20 nm band pass filter (Edmund Optics). For all fluorescence measurements, the exposure time was set to 100 ms. Fluorescence images were processed with Image J.[5]
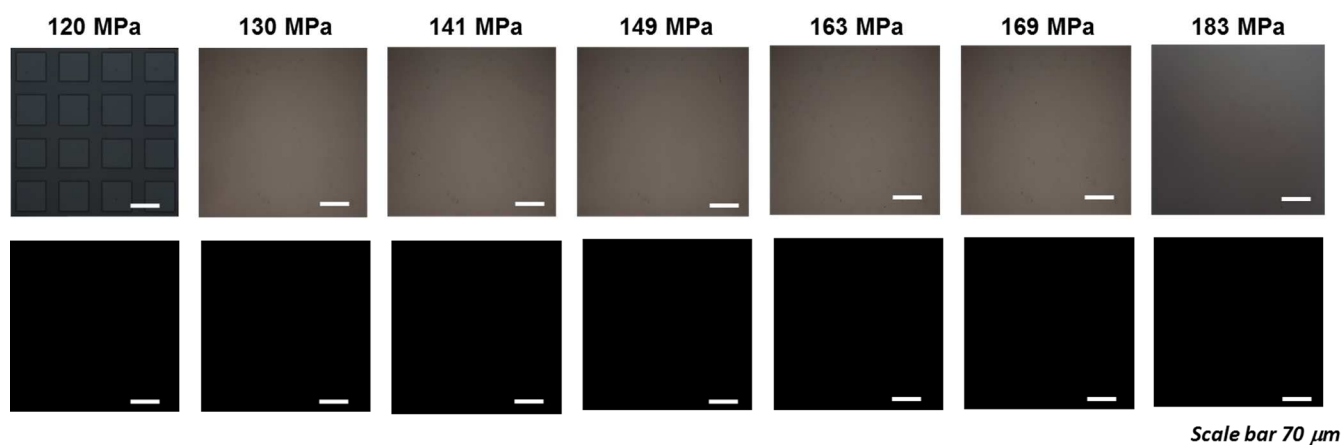

Scale bar 70 μm

Figure S1. Representative optical and fluorescence micrographs of a control specimen with non-covalently bonded epoxy layers following laser impingement with increasing laser intensity.
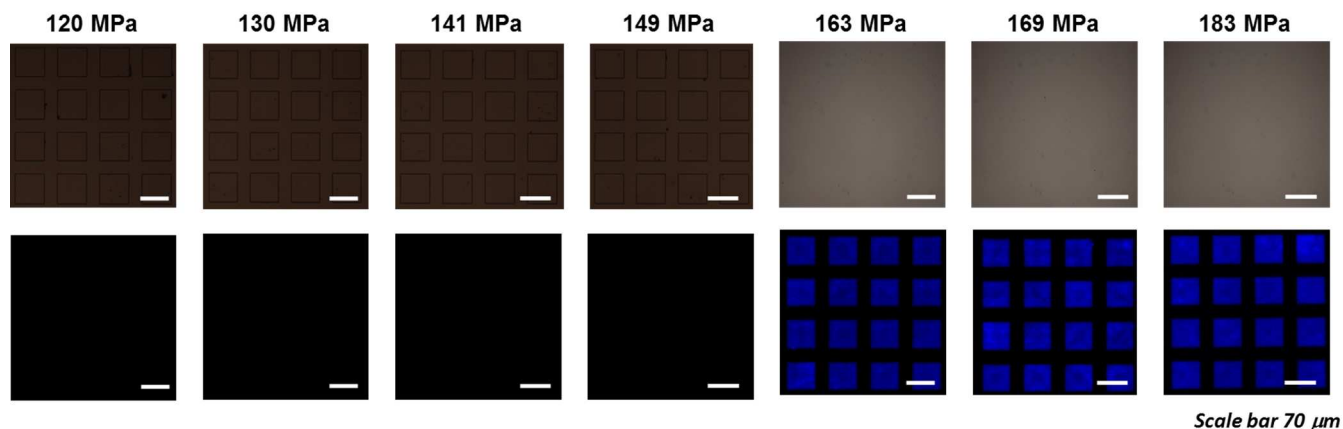
Figure S2. Representative optical and fluorescence micrographs of an active specimen with covalently bonded epoxy layers following laser impingement with increasing laser intensity.

5. ToF-SIMS Imaging and XPS

Active specimens were subjected to an interfacial stress of 163 MPa and subsequently analyzed with ToF-SIMS (Physical Electronics PHI Trift III) imaging and XPS spectroscopy. For ToF-SIMS imaging, Au liquid source run with Au^+ ion under static mode accelerated at 22 KeV energy was used as the source. Data were collected for 10 minute duration. The same specimens were analyzed with XPS spectroscopy to compare N 1S intensity at locations inside and outside of the square array. XPS measurements were performed using a Kratos Axis ULTRA with monochromated Al Kα X-ray source (15 µm spot). The kinetic energy of the electrons was measured by a 180° hemispherical energy analyzer operated in the constant analyzer energy mode (CAE) at 50 eV pass energy for elemental spectra. Measured spectra were fit with Voigt profiles and calibrated by centering SiO_2 2P peak at 103.5 eV. All data were normalized to the SiO_2 2p peak.

6. Patterned Anthracene Reference Sample Preparation

Patterned anthracene reference samples (Scheme S1) were prepared to compare the degree of activation with active specimens. Fused silica substrates (1.5 mm thick, GM associates) were cleaned in piranha solution at 120 °C for 30 minutes. The cleaned substrates were washed with DI water, dried in a stream of air, and then further dried in a convection oven at 120 °C for 30 min. Functionalized fused silica substrates were prepared by immersing cleaned substrates in a 10 mM toluene solution of 9-anthracenyltrimethoxysilane (Gelest). For full functionalization, samples were kept in a sealed container for 24h on a benchtop. After 24h, the substrates were sonicated in toluene and subsequently rinsed with toluene, isopropyl alcohol, and DI water followed by drying under a stream of air. The patterned anthracene surface was fabricated by photo patterning a photoresist (AZ 5214 E, microChem) and removal of exposed anthracene with oxygen plasma. After oxygen plasma treatment, residual photoresist was removed by rinsing with N-methyl-2-pyrrolidone. Fluorescence intensity was measured under identical conditions as the activated mechanophore specimens.
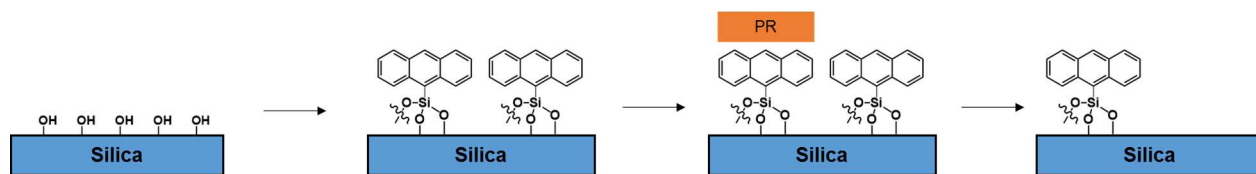
Scheme S1. Preparation of patterned anthracene reference sample on silica surface

7. XPS Characterization of Active Specimens

  The change in surface chemistry during active specimen fabrication was confirmed with XPS. XPS was measured with the same method mentioned in section above. Measured spectra were fit with Voigt profiles and calibrated by centering SiO_2 2P peak at 103.5 eV.   All data were normalized to the SiO_2 2p peak.
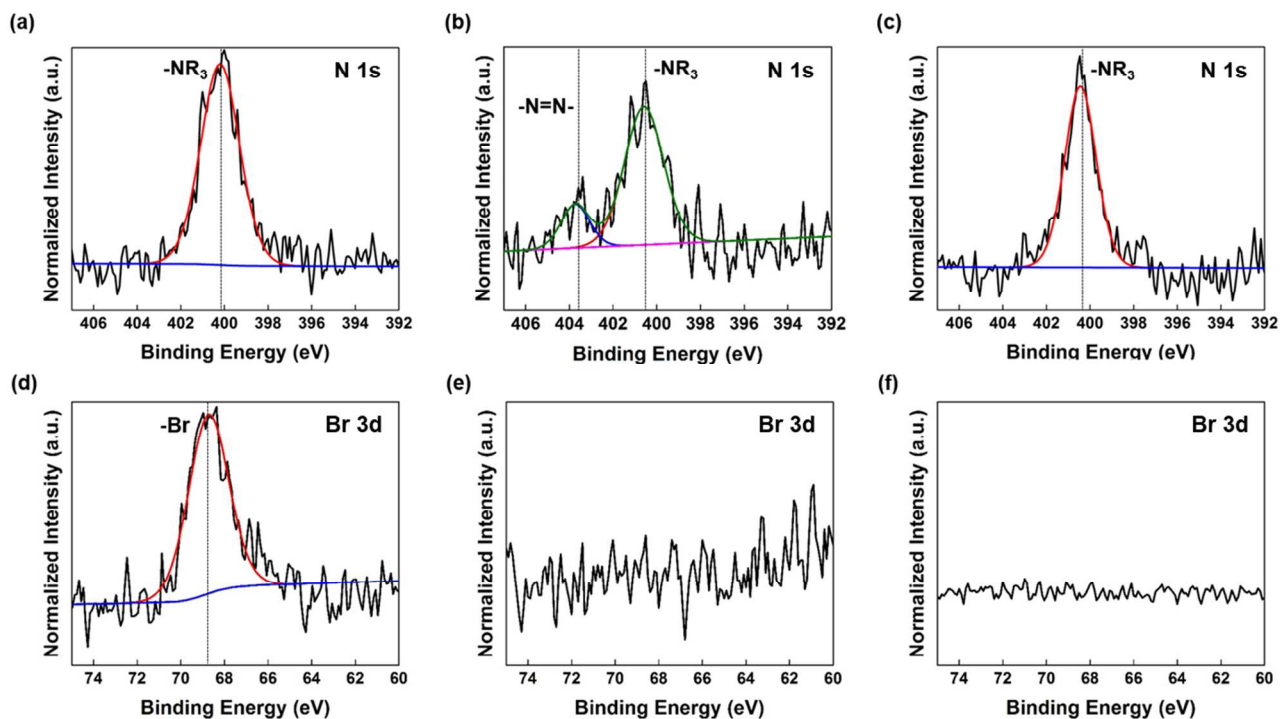

Figure S3. N 1s and Br 3d XPS spectrum: (a, d) Bromine terminated mechanophore immobilized on fused silica, (b, e) after reaction with sodium azide, (c, f) after reaction with triphenylphosphine.

8. Laser-Induced Stress Wave Activation of Mechanophore Functionalized Interfaces

Maleimide-anthracene mechanophore-functionalized specimens were prepared for the laser-induced stress wave experiment following the steps described in section 3. The sample dimensions are summarized in Figure S4. An epoxy film (1.5 μm thick) was patterned in 75x75μm squares on a maleimide-anthracene functionalized fused silica (1.5 mm) with aluminum energy absorbing layer (400 nm) and sodium silicate confining layer (1 μm) on the opposite side.

The setup for generating laser-induced stress waves is shown schematically in Figure S4. High amplitude short duration acoustic waves were generated in the specimen by impinging a Nd:YAG pulse laser on the Al energy absorbing layer. The Al layer is confined by the sodium silicate layer. Therefore, the rapid expansion of the Al results in a compressive acoustic wave that propagates through the fused substrate towards the epoxy film. After reflecting off the free surface of the epoxy, the mechanophore mediated interface between the epoxy and fused silica substrate is loaded in tension. When the magnitude of the stress exceeds the interfacial strength, the epoxy film spalls from the substrate.
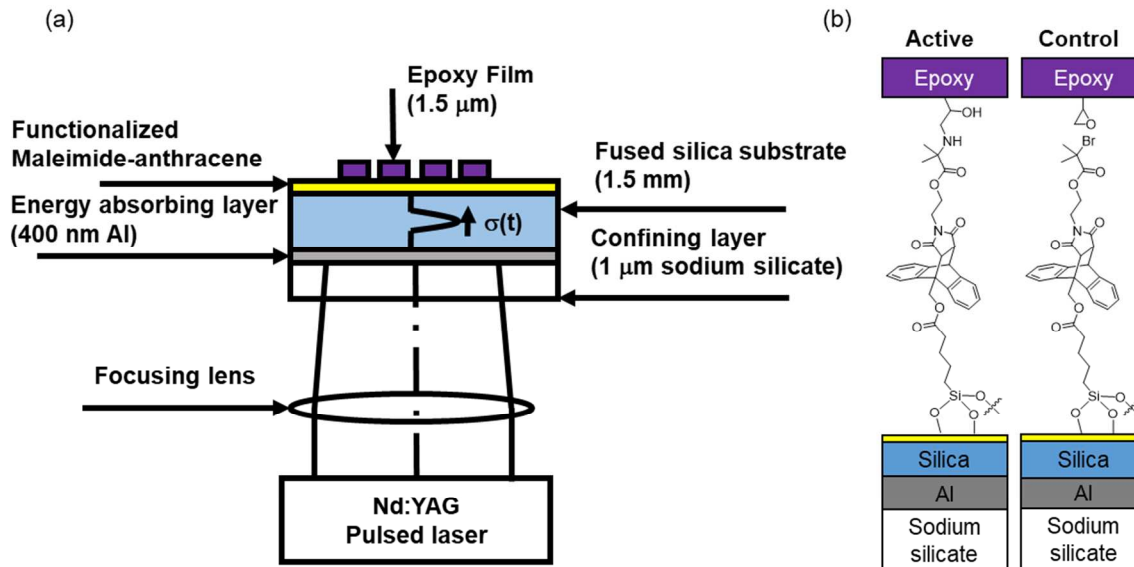
Figure S4. Schematic representations of (a) the experimental setup for laser-induced stress wave activation of mechanophore functionalized interface, and (b) the fused silica-epoxy interface comprising the maleimide-anthracene mechanophore, which is covalently bonded (active specimen). Specimens with non-covalent bonding between bromine-terminated mechanophore and epoxy layer were also prepared as a control.

Active and control samples were both tested to examine the role of covalent bonding in mechanophore activation. Laser fluence was varied incrementally between 53 mJ/mm^2 and 90 mJ/mm^2 by adjusting the energy of the Nd:YAG laser while keeping the beam diameter constant at 1.5 mm. The interface stress was calculated using a calibration procedure. (See below)

9. Calibration Procedure Using Aluminum Blanket Film

A series of calibration experiments were executed to determine the interfacial strength at film failure, as described in detail by Grady et al.[6] The substrate stress and interface stress generated

for a given Nd-YAG laser intensity are determined using a set of calibration specimens with reflective 100 nm thick Al films (rather than epoxy) deposited on top of a 1.5 mm thick fused silica substrate (Figure S5). The thin Al films do not spall and provide a high signal to noise ratio for interferometric measurement. A 400 nm thick Al energy absorbing layer with 1000 nm thick sodium silicate confining layer was deposited on top on the opposite side.
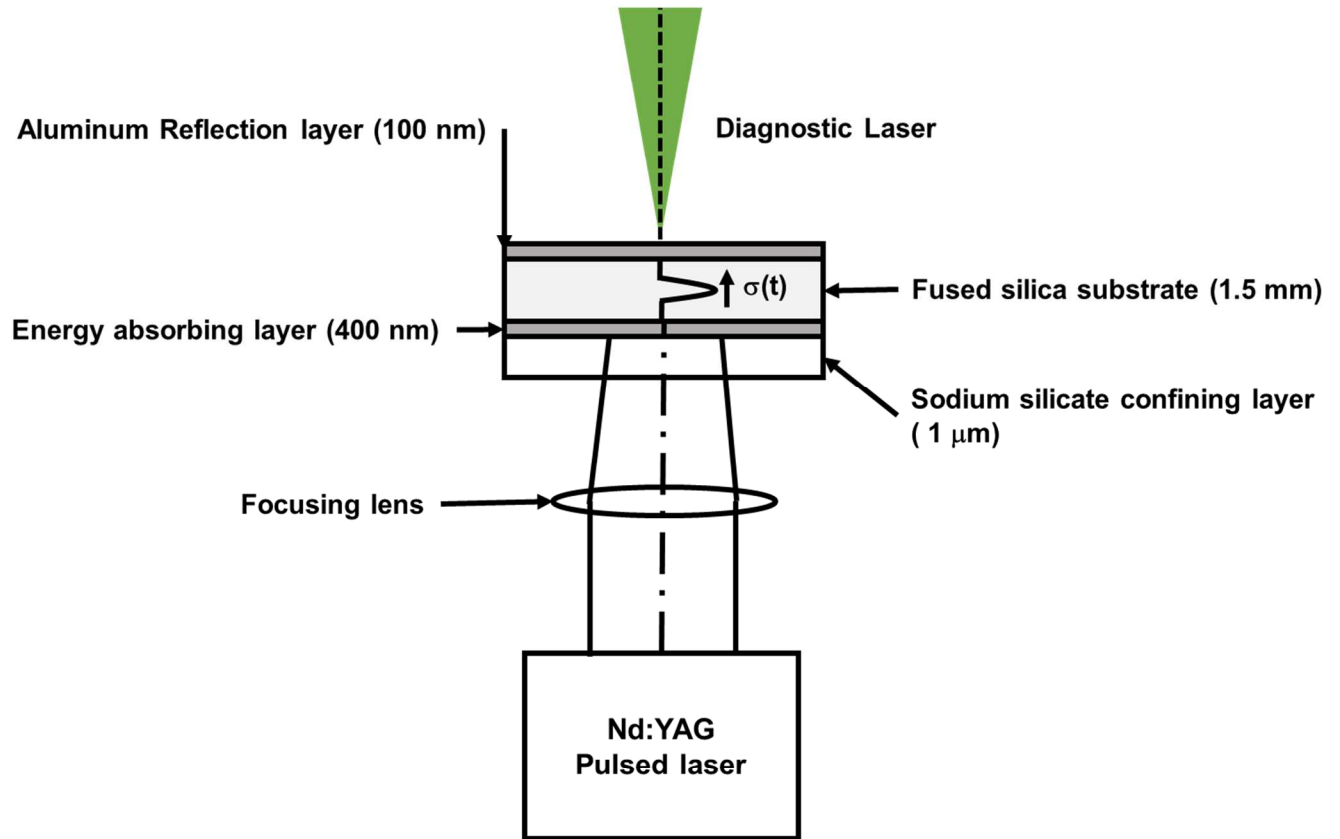

Figure S5. Schematic of aluminum blanket film for calibration protocol.

For systematic variation in laser intensity, the displacement of the Al reflecting film free surface was measured using Michelson interferometer with a 532 nm laser diagnostic beam. The resulting interference voltage signal was measured using a silicon photodetector (Electro-Optics Technology ET-2030) connected to a 40 GHz oscilloscope (LeCroy LC584 A). Displacement of

the free surface and substrate stress (as described previously by Grady et al.[6]) was calculated using the voltage signal (Fig. S7).

Interface stress between the functionalized substrate and epoxy film was then calculated with 1D finite element model. The substrate and film were discretized using two-node, linearly elastic 1D elements and an explicit central difference time step. The compressive substrate stress pulse measured during experimental calibration is used as input for the model. The model applies the input stress in the substrate near the interface and stress development at the interface is calculate. Parameters used for substrate stress and interface stress are summarized in Table S1.

Table S1. Material properties used to calculate substrate and interface stress.

Material	Young's modulus (Gpa)	Density (kg/m^3)	Poisson's ratio
Fused Silica	78	2200	0.42
Epoxy	2.5	608	0.33

Figure S6 shows fringe data for a representative fused silica calibration sample tested at a laser intensity of 53 mJ/mm^2. For each laser intensity, five separate interferometry measurements were carried out. The laser fluence was varied from 53 mJ/mm^2 to 92 mJ/mm^2. The calculated interface stress is shown in Figure S7 as a function of laser intensity.
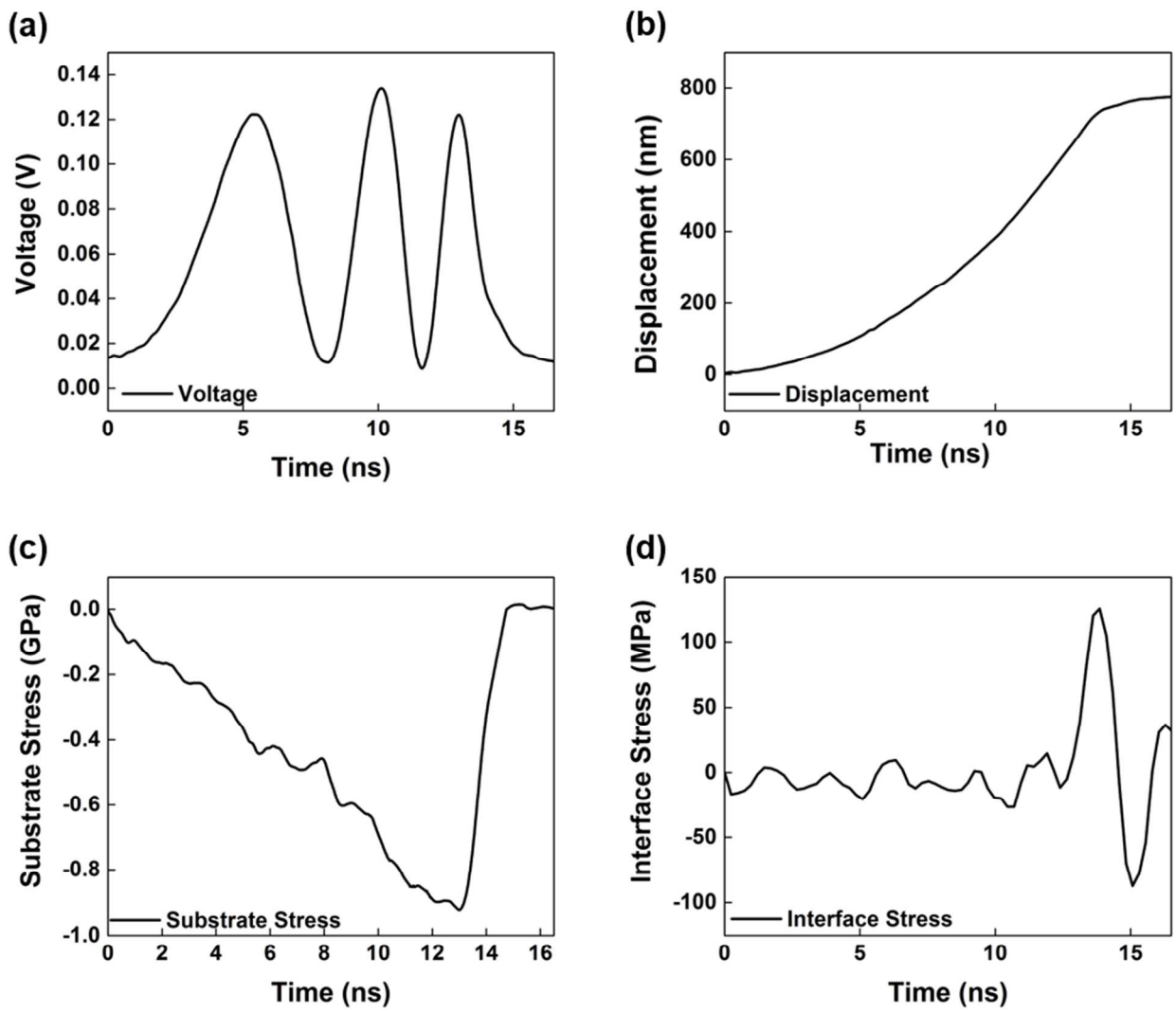
Figure S6. Representative interferometric data obtained from laser-induced stress wave: (a) photodetector fringe data, (b) displacement (c) substrate stress, (d) interface stress.
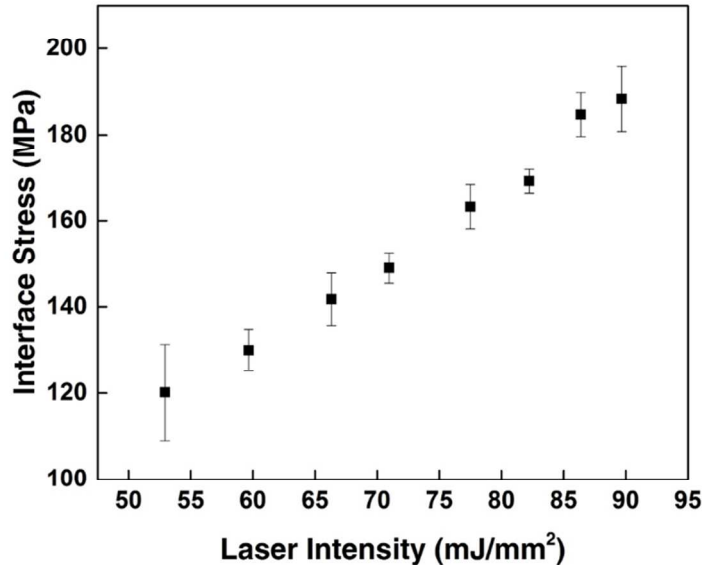
Figure S7. Interface stress applied at epoxy-fused silica as a function of loaded Nd-YAG laser intensity.

11. References

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