Supporting Information for

Empowering Self-Reporting Polymer Blends with Orthogonal Optical Properties Responsive at Broader Force Range

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1. General Experimental Details

Materials. Unless otherwise stated, all regents were purchased from commercial sources and used without further purification. All reactions were performed under argon atmosphere unless otherwise specified, and all glass wares were oven dried before use. 5,5'/7'-(2-Hydroxyethylenoxy)adamantylideneadamantane 1,2-dioxetane (**Ad**), 3'-(ethyl(2-hydroxyethyl)amino)-6'-(ethylamino)-2-(2-hydroxyethyl)-2',7'-dimethylspiro-[isoindoline-1,9'-xanthen]-3-one (**Rh**) were prepared according to the previous literatures.^{*S1,S2*} Polytetramethylene glycol (**PTMG**: Mn = 650 g/mol) was dried at 70 °C under vacuum for 2 hours before use. Chloroform (CHCl₃) was distilled under argon over CaH₂ prior to use.

Characterization methods. Liquid ¹H NMR spectra were recorded in CDCl₃ solvent on a Bruker AVANCE III-400 spectrometer. Differential scanning calorimetry (DSC) measurements were conducted using the TA Instruments Q-20 with a scan rate of 10 °C/min under nitrogen atmosphere. Field emission scanning electron microscopies (FE-SEM) were carried out using a Hitachi Limited model SU800 microscope operating at an accelerating voltage of 3.0 kV. Gel Permeation Chromatography (GPC) of the PU samples was carried out an Agilent PL-GPC50 with multi detectors, using tetrahydrofuran (THF) as an eluent with a flow rate of 1.0 mL/min. The molecular weights of the tested polymers were determined by the light scattering detector. UV-vis absorption spectra were obtained on a PerkinElmer Lamda 750 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. High resolution transmission electron microscopies (HR-TEM) were performed on a JEOL model JEM-2100 plus microscope operating at an accelerating voltage of 200 kV. The ultrathin specimens were prepared by LEICA EM UC7.

Testing of mechanochromism. Tensile experiments were carried out on a TA Rheometrics, DHR-2 equipped with an Xpansion Instruments, SER3, extensional fixture. Optical images were captured by Nikon D5500 with 18-55mmf/3.5-5.6G VR lens under ambient room light (Figure S15a). The pictures were taken every 20 ms from the starting point of each tensile test. The dimension of the strips used for tensile tests was $30 \times 5.3 \times (0.20 \pm 0.03)$ mm.

Optomechanical testing. Tensile experiments were carried out on a TA Rheometrics, DHR-2 equipped with an Xpansion Instruments, SER3, extensional fixture. The two rotating drums of the fixture are colored black by permanent marker to eliminate reflecting light. The pco.edge 5.5 camera equipped with a Nikon AF NIKKOR 50 mm 1:1.4D lens was used to record videos in darkness (Figure S15b). All the videos were recorded in the rolling shutter color mode with a shooting rate of 200 fps and exposure time of 5.00 ms. The frames of the resulting video were exported as separate monochrome TIF-files and light intensity was analyzed with a homemade program in MATLAB as literature.^{S3} The total intensity for a dark image as the noisy signal was subtracted from all film intensities. The dimension of the strips used for tensile tests was $30 \times 5.3 \times (0.20 \pm 0.03)$ mm.

RGB color analysis

The RGB value was obtained by analyzing images in MATLAB software. RGB ratios

of each image was calculated using Grassmann's law.

$$r = \frac{R}{R+G+B}; \ g = \frac{G}{R+G+B}; \ b = \frac{B}{R+G+B}$$

r, *g*, and *b* are the red, green and blue component of the RGB ratio, respectively. R, G and B are the average intensity of red, green and blue channels in the region of interest.

2. Synthetic Procedures for PU/PLLA Blends

Synthesis of dual mechano-responsive linear polyurethane (Rh-Ad-PU).

The dibutyltin dilaurate (17 μ L) in 2 mL CHCl₃ was added to a mixture of diphenylmethane-diisocyanate (MDI, 1.45g, 5.79 mmol), 5,5'/7'-di(2-hydroxyethylenoxy) adamantylideneadamantane 1,2-dioxetane (Ad, 109.82 mg, 0.26 mmol), 3'-(ethyl(2hydroxyethyl)amino)-6'-(ethylamino)-2-(2-hydroxyethyl)-2',7'-dimethylspiro[isoindoline-1,9'-xanthen]-3-one (Rh, 131.0 mg, 0.26 mmol) and CHCl₃ (10 mL), the solution was stirred 30 min at 30°C under an argon atmosphere. Then the polytetramethylene glycol (PTMG, $M_n = 650$ g/mol, 3.4g, 5.23 mmol) in CHCl₃ (10 mL) was added. After stirring for another 1.5 hours at 45 °C, the reaction mixture was cooled down to room temperature and precipitated into *n*-hexane. The precipitate was collected and dried in vacuo at room temperature to afford Rh-Ad-PU as off-white rubbery solid (Mn = 62.0 kDa, Mw = 207.5kDa, PDI = 3.35, Figure S1). The chemical compositions of the Rh-Ad-PU were determined by ¹H NMR (Figure S2). Rh and Ad were successfully coupled into polyurethane chains in a covalent way, as confirmed by the appearance of characteristic peaks at 8.00 and 2.82 ppm, respectively.

Synthesis of dual mechano-responsive linear polyurethanes (Rh-PU or Ad-PU).

The dibutyltin dilaurate (9 μ L) in 1 mL CHCl₃ was added to a mixture of diphenylmethane-diisocyanate (MDI, 0.69g, 2.77 mmol), 5,5'/7'-di(2-hydroxyethylenoxy) adamantylideneadamantane 1,2-dioxetane (Ad, 54.91 mg, 0.13 mmol) or 3'-(ethyl(2hydroxyethyl)amino)-6'-(ethylamino)-2-(2-hydroxyethyl)-2',7'-dimethylspiro[isoindoline-1,9'-xanthen]-3-one (Rh, 65.5 mg, 0.13 mmol) and CHCl₃ (5 mL), the solution was stirred 30 min at 30 °C under an argon atmosphere. Then the polytetramethylene glycol (PTMG, $M_{\rm n} = 650$ g/mol, 1.7 g, 2.62 mmol) in CHCl₃ (5 mL) was added. After stirring for another 1.5 hours at 45 °C, the reaction mixture was cooled down to room temperature and precipitated into *n*-hexane. The precipitate was collected and dried in vacuo at room temperature to afford **Rh-PU** or **Ad-PU** as off-white rubbery solid (**Rh-PU**, *M*n = 83.1 kDa, *M*w = 328.1 kDa, PDI = 3.95; Ad-PU, *M*n = 72.3 kDa, *M*w = 172.2 kDa, PDI = 2.38, Figure S1). The chemical compositions of the Rh-PU or Ad-PU were determined by ¹H NMR (Figure S3-S4). Rh or Ad were successfully coupled into polyurethane chains in a covalent way, as confirmed by the appearance of characteristic peaks at 8.00 or 2.82 ppm, respectively.

Synthesis of control linear polyurethane (L-Blank-PU).

The dibutyltin dilaurate (17 μ L) in 2 mL CHCl₃ was added to a mixture of diphenylmethane-diisocyanate (MDI, 1.45g, 5.79 mmol), and CHCl₃ (10 mL). Then the polytetramethylene glycol (PTMG, $M_n = 650$ g/mol, 3.74g, 5.75 mmol) in CHCl₃ (10 mL) was added. After stirring for another 1.5 hours at 45 °C, the reaction mixture was cooled down to room temperature and precipitated into *n*-hexane. The precipitate was collected and dried in vacuo at room temperature to afford **L-Blank-PU** as off-white rubbery solid (Mn = 142.4 kDa, Mw = 333.96 kDa, PDI = 2.35, Figure S1).

Synthesis of low molecular weight polylactic acid (PLLA).

PLLA was prepared via one-step ring-open polymerization. L-lactide (1.66 g, 11.5 mmol) and 1,4-butanediol (45.06 mg, 0.5 mmol) were added into a two-necked flask under argon atmosphere. After heating to 125 °C, the mixture was melted. Then, Sn(Oct)₂ (13.98 mg, 0.035 mmol) with tetrafluoride tablets was added and the reaction was kept at 160 °C for 2 hours. The reaction mixture was cooled down to room temperature, followed by adding dichloromethane. The mixture was then deposited in cold methanol. The precipitate was collected and dried in vacuo at room temperature to afford **PLLA** as a white solid powder (1.0 g). The molecular weight of **PLLA** ($M_n = 4.3$ kDa) was characterized by ¹H-NMR as shown in Figure S5 and calculated through formula.^{S4}

$$Mn = \left(\frac{l_1}{l_2} + 1\right) * 72 * 2 + 90 \tag{1}$$

Where I_1 and I_2 are the areas of peaks 1 and 2, respectively, 72 is the molar mass of one lactic acid repeat unit, and 90 is the total molar mass of the rest part of the molecule. General preparation method of PU/PLLA blend polymer films.

The as-prepared **Rh-Ad-PU**, **Rh-PU**, **Ad-PU** or **L-Blank-PU** respectively, was added to tetrahydrofuran (THF) and stirred until a uniform solution was obtained. Meanwhile, different amount of **PLLA** (Table S1) were added into THF respectively and stirred until the powders were fully dissolved. Then, the two polymer solutions were mixed together and stirred for 3 hours before poured into a Teflon mould ($50 \times 30 \times 10$ mm). THF was evaporated under ambient conditions followed by vacuum drying of the films at room temperature for 12 hours. The removal of THF was confirmed by DSC analyses (Figure S9).

3. <u>Supplementary Table</u>

Samples	Rh-Ad-PU (mg)	PLLA diol (mg)	PLLA Contents (wt%)	L-Blank-PU (mg)
PU/PLLA-0%	400	0	0	0
PU/PLLA-5%	400	21	5	0
PU/PLLA-10%	400	45	10	0
PU/PLLA-20%	400	100	20	0
Control-PU/PLLA-10%	0	45	10	400
Rh-PU/PLLA-10%	400	45	10	0
Ad-PU/PLLA-10%	400	45	10	0

4. <u>Supplementary Figures</u>



Figure S1. The GPC traces of Rh-Ad-PU; Rh-PU; Ad-PU and L-Blank-PU.



Figure S2. ¹H NMR spectrum of the Rh-Ad-PU in CDCl₃.



Figure S3. ¹H NMR spectrum of the Rh-PU in CDCl₃.



Figure S4. ¹H NMR spectrum of the Ad-PU in CDCl₃.



Figure S5. ¹H NMR spectrum of the PLLA in CDCl₃.



Figure S6. Images of the ruptured Rh-Ad-PU film: (a) under daylight and (b) in the dark.



Figure S7. UV-vis transmittance of **Rh-Ad-PU** and its blended films. Insert shows four pieces of films on a labeled paper.



Figure S8. TEM images of ultrathin specimens (thickness: ca. 50 nm) cut at cryogenic conditions from bulk samples of (a) **PU/PLLA-0%** (scale: 500 nm); (b) **PU/PLLA-5%** (scale: 2 μm); (c) **PU/PLLA-10%** (scale: 2 μm) and (d) **PU/PLLA-20%** (scale: 2 μm).



Figure S9. DSC curves of PLLA, Rh-Ad-PU and its blends (The glass transition temperature is obtained by TA data processing software).



Figure S10. (a) UV-vis absorption spectrum of a **PU/PLLA-10%** film after stretching; (b) FL spectra of a **PU/PLLA-10%** film before and after stretching (Excitation wavelength: 420 nm). The ruptured film exhibited absorption at 420 nm and emitted red fluorescence, due to the existence of ring opened **Rh**,^{*S2*} that showed its potential as the fluorescent acceptor of excited adamantone ($\lambda_{em} = 420 \text{ nm}$). ^{S5}



Figure S11. RGB analysis for blends of (a) PU/PLLA-0% (b) PU/PLLA-5% (c) PU/PLLA-10% (d) PU/PLLA-20%. All the tests were conducted under daylight lamp.



Figure S12. RGB analysis for **Control-PU/PLLA-10%** at (a) 0.2 s^{-1} (b) 1.0 s^{-1} (c) 5.0 s^{-1} strain rate. All the tests were conducted under daylight lamp. The illustrations are the pictures of the fractured blends.



Figure S13. SEM images of PU/PLLA-10% surface (a) before and (b) after stretching.



Figure S14. (a) Stress and the intensity in green channel as a function of strain (The **Rh-PU/PLLA-10%** film was stretched at a strain rate of 0.2 s⁻¹). (b) Stress and cumulative light intensity as a function of strain (The **Ad-PU/PLLA-10%** film was stretched at a strain rate of 0.2 s⁻¹).



Figure S15. Setups for the mechanochromic and mechanoluminescent tests recorded (a) under daylight; (b) in the dark.

5. <u>References</u>

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