Electronic Supplementary Material (ESI) for Polymer Chemistry.


# An Optomechanical Study of Mechanoluminescent Elastomeric Polyurethanes with Different Hard Segments

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## Experimental Procedures

**Materials.** Unless otherwise stated, all reagents and solvents were purchased from Sigma-Aldrich, TCI or Tianjin Jiangtian Chemical Company and used without further purification. 5,5'/7'-(2-Hydroxyethylenoxy) adamantylideneadamantane 1,2-dioxetane **(MP)**, 4,7-di(thiophen-2-yl) benzo[*c*][1,2,5]thiadiazole and polyurethane (PU) were prepared according to literature procedures.[1,2] Polytetrahydrofuran (PTMG: $M_n$ = 650 g/mol) was dried at 70 $^oC$ under vacuum for 2 h before use. Chloroform ($CHCl_3$) was distilled under argon atmosphere over $CaH_2$ prior to use. All the reactions were performed under argon atmosphere unless otherwise specified, and all glassware were dried in the oven before use.

## Characterization Methods.

Analytical gel permeation chromatography (GPC) analyses were performed on a Shimadzu LC10-AT using polystyrene as the standard, and THF as an eluent at a flow rate of 1.0 mL/min. FT-IR spectra were collected in reflection mode on a Bruker Alpha spectrometer with a scan range of 500-4000 $cm^{-1}$. DSC (TA DSC-Q20) measurements were performed under nitrogen atmosphere at a heating or cooling rate of 10 $^oC$/min. X-ray diffractometer (XRD) experiments were carried out on Rigaku SmartLab X-ray diffractometer. The two-dimensional (2D) SAXS experiments were carried out on a GANESHA 300XL+ system from JJ X-ray in the X-ray lab at DSM Materials Sciences Center (DMSC). The instrument is equipped with a Pilatus 300K detector, with pixel size of 172μm*172μm. The X-ray source is a Genix 3D

Microfocus Sealed Tube X-Ray Cu-source with integrated Monochromator (multilayer optic "3D version" optimized for SAXS) (30W). The wavelength used is λ=1.5418Å. The detector moves in a vacuum chamber with sample-to-detector distance varied between 0.115m and 1.47m depending on the configuration used, as calibrated using silver behenate ($d_{001}$=58.380 Å). The minimized background scattering plus high-performance detector, allows for a detectable q-range varying from 0.003 to 3$Å^{-1}$ (0.2 to 210 nm). Field emission scanning electron microscopies (FE-SEM) were performed on a Hitachi Limited model SU800 microscope. Optical microscopic images were recorded on a Nikon microscope (ECLIPSE LV100ND). Cyclic tensile experiments were carried out on E1-F1-G1 of INSTRON.

**General Procedure for Synthesis of PUs**.

**UHDI-1. MP** (64.7 mg, 0,1538 mmol) and DBTDL (5 µL) in 2 mL $CHCl_3$, HDI (756.76 mg, 4.4992 mmol) in 3 mL $CHCl_3$, PTMG (2.81g, 4.323 mmol) in 15 mL $CHCl_3$ were used with polymerization time ca.4.5 h. $M_n$ = 105 kDa, $Đ$ = 1.8.

**UHDI-2. MP** (64.7 mg, 0,1538 mmol) and DBTDL (5 µL) in 2 mL $CHCl_3$, HDI (756.76 mg, 4.4992 mmol) in 3 mL $CHCl_3$, PTMG (2.81g, 4.323 mmol) in 15 mL $CHCl_3$ were used with polymerization time ca.6 h. $M_n$ = 136 kDa, $Đ$ = 1.8.

**UTDI-1. MP** (64.7 mg, 0,1538 mmol) and DBTDL (5 µL) in 2 mL $CHCl_3$, TDI (783.58 mg, 4.4992 mmol) in 3 mL $CHCl_3$, PTMG (2.81g, 4.323 mmol) in 15 mL $CHCl_3$ were used with polymerization time ca.3.5 h. $M_n$ = 70 kDa, $Đ$ = 1.8.

**UTDI-2. MP** (64.7 mg, 0,1538 mmol) and DBTDL (5 µL) in 2 mL $CHCl_3$, TDI

(783.58 mg, 4.4992 mmol) in 3 mL $CHCl_3$, PTMG (2.81g, 4.323 mmol) in 15 mL $CHCl_3$ were used with polymerization time ca.4 h. $M_n$ = 109 kDa, $Đ$ = 1.8.

**UTDI-3. MP** (64.7 mg, 0,1538 mmol) and DBTDL (5 µL) in 2 mL $CHCl_3$, TDI (783.58 mg, 4.4992 mmol) in 3 mL $CHCl_3$, PTMG (2.81g, 4.323 mmol) in 15 mL $CHCl_3$ were used with polymerization time ca.6.5 h. $M_n$ = 132 kDa, $Đ$ = 1.9.

**UPPDI. MP** (64.7 mg, 0,1538 mmol) and DBTDL (5 µL) in 2 mL $CHCl_3$, PPDI (720.45 mg, 4.4992 mmol) in 3 mL $CHCl_3$, PTMG (2.81g, 4.323 mmol) in 15 mL $CHCl_3$ were used with polymerization time ca.4 h. $M_n$ = 109 kDa, $Đ$ = 1.7.

**UIPDI. MP** (64.7 mg, 0,1538 mmol) and DBTDL (5 µL) in 2 mL $CHCl_3$, PPDI (1045 mg, 4.4992 mmol) in 3 mL $CHCl_3$, PTMG (2.81g, 4.323 mmol) in 10 mL $CHCl_3$ were used with polymerization time ca.4.5 h. $M_n$ = 105 kDa, $Đ$ = 1.9.

**UMDI. MP** (64.7 mg, 0,1538 mmol) and DBTDL (5 µL) in 2 mL $CHCl_3$, PPDI (1125.8 mg, 4.4992 mmol) in 3 mL $CHCl_3$, PTMG (2.81g, 4.323 mmol) in 25 mL $CHCl_3$ were used with polymerization time ca.3.5 h. $M_n$ = 100 kDa, $Đ$ = 1.7.

**General preparation process of PU films.**

The polymer films of **UHDIs**, **UTDIs**, **UPPDI**, **UIPDI** and **UMDI** were prepared as follows. 1.5 g of polymers and 3 mg 4,7-di(thiophen-2-yl) benzo[*c*][1,2,5]thiadiazole as chemiluminescent acceptors were dissolved in 20 mL THF. Films were prepared by drop casting the mixture solution to a Teflon mold (105×45×5 mm) followed by slowly evaporating solvent in ambient condition prior to use. Films for cyclic tensile tests were cut into rectangles of 18×6 mm using a Zwick ZCP 020 manual cutting

press equipped with a cutting blade of 6 mm width. Films for optomechanical tests were cut into rectangles of 25×2.5 mm using a Zwick ZCP 020 manual cutting press equipped with a cutting blade of 2.5 mm width. The thickness of the films was 0.22 ± 0.01 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. All the videos were recorded in the rolling shutter color mode with a shooting rate of 200.35 fps and exposure time of 4.98 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. The total intensity for a dark image as the noisy signal was subtracted from all film intensities.

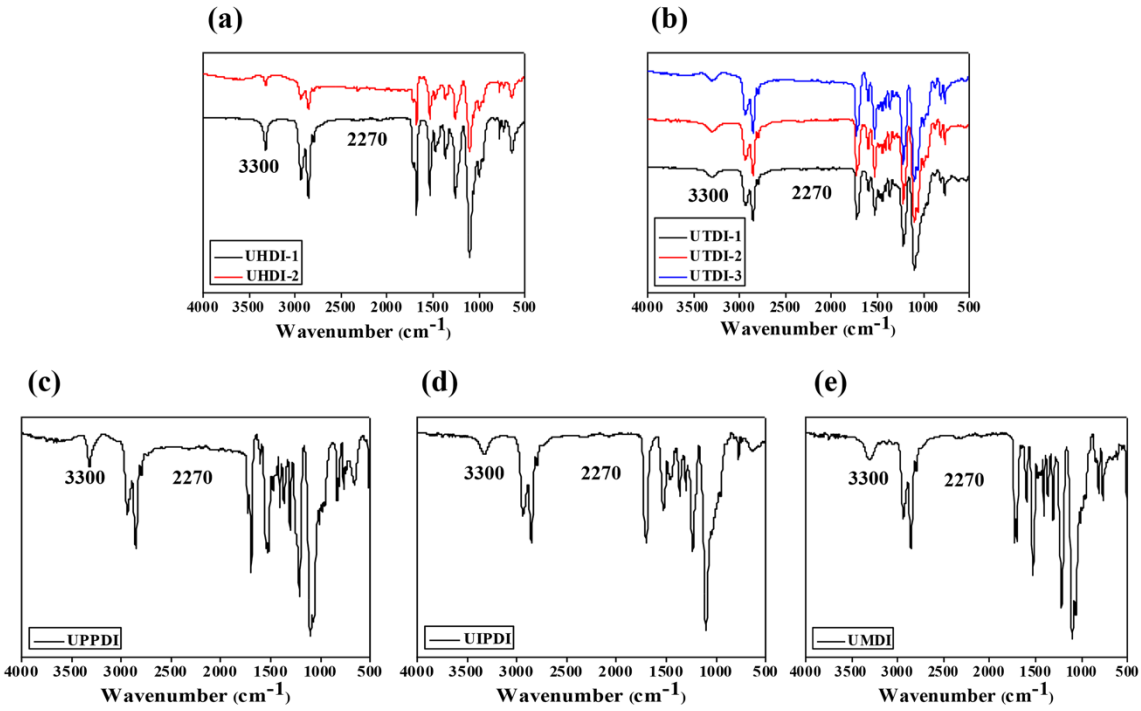


**Fig. S1** FT-IR spectra of (a) **UHDIs**, (b) **UTDIs**, (c) **UPPDI**, (d) **UIPDI** and (e) **UMDI**.

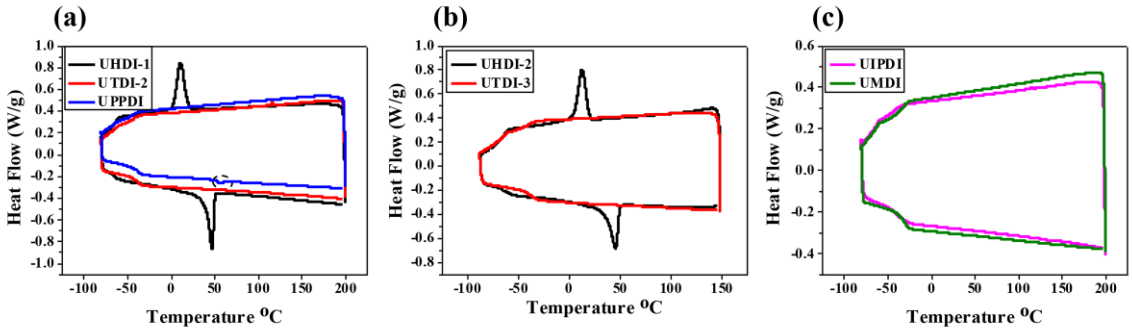


**Fig. S2** (a) DSC curves of **UHDI-1**, **UTDI-2** and **UPPDI** films. (b) DSC curves of **UHDI-2** and **UTDI-3** films. (c) DSC curves of **UIPDI** and **UMDI** films.

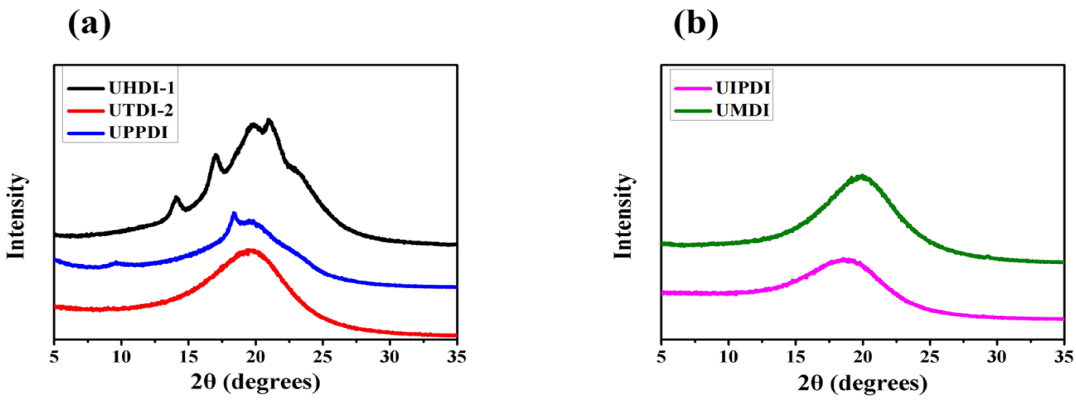


**Fig. S3** (a) X-ray diffraction profiles of **UHDI-1**, **UTDI-2** and **UPPDI** films. (b) X-ray diffraction profiles of **UIPDI** and **UMDI** films.

**Table S1** Structure parameters of polyurethanes obtained by SAXS analysis.

| | $q_{max}$ (Å$^{-1}$) | $D$ (nm) | $l_{HS}$ (nm) | $l_{SS}$ (nm) | $L$ (nm) | $f_{HS}$ |
|---|---|---|---|---|---|---|
| **UHDI-1** | 0.082 | 7.66 | 3.16 | 5.44 | 8.6 | 0.23 |
| **UPPDI** | 0.194 | 3.24 | 1.86 | 5.64 | 7.5 | 0.18 |

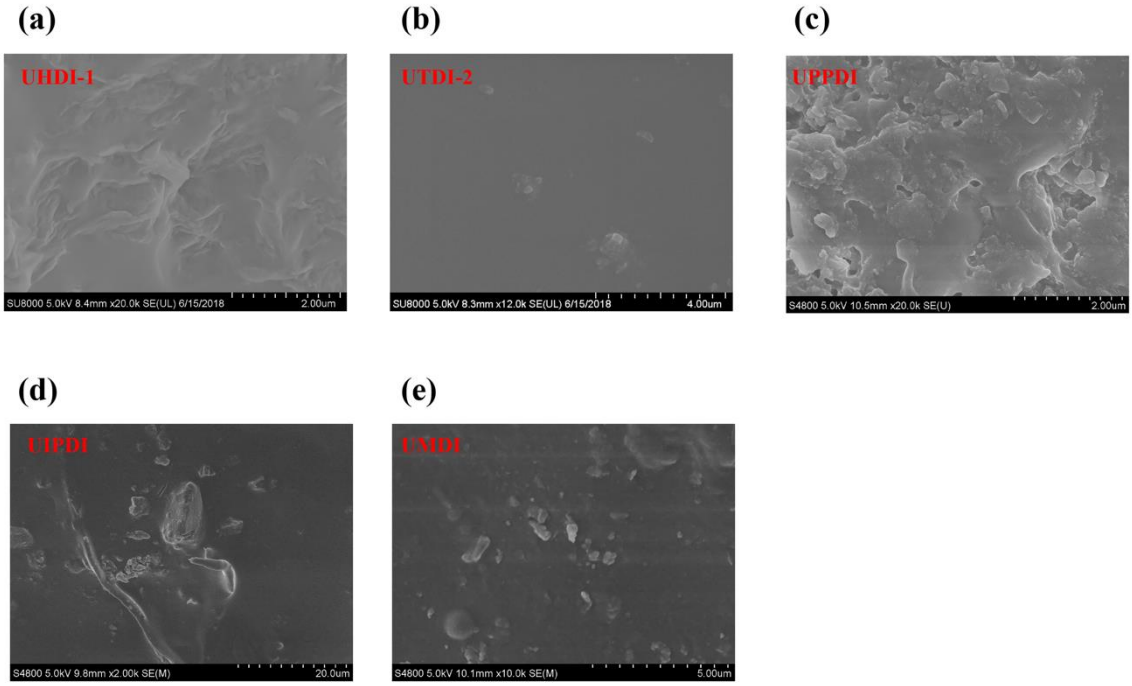


**Fig. S4** SEM images of (a) **UHDI-1**, (b) **UTDI-2**, (c) **UPPDI**, (d) **UIPDI**, (e) **UMDI**.

**Fig. S5** Setup for the optomechanical tests.

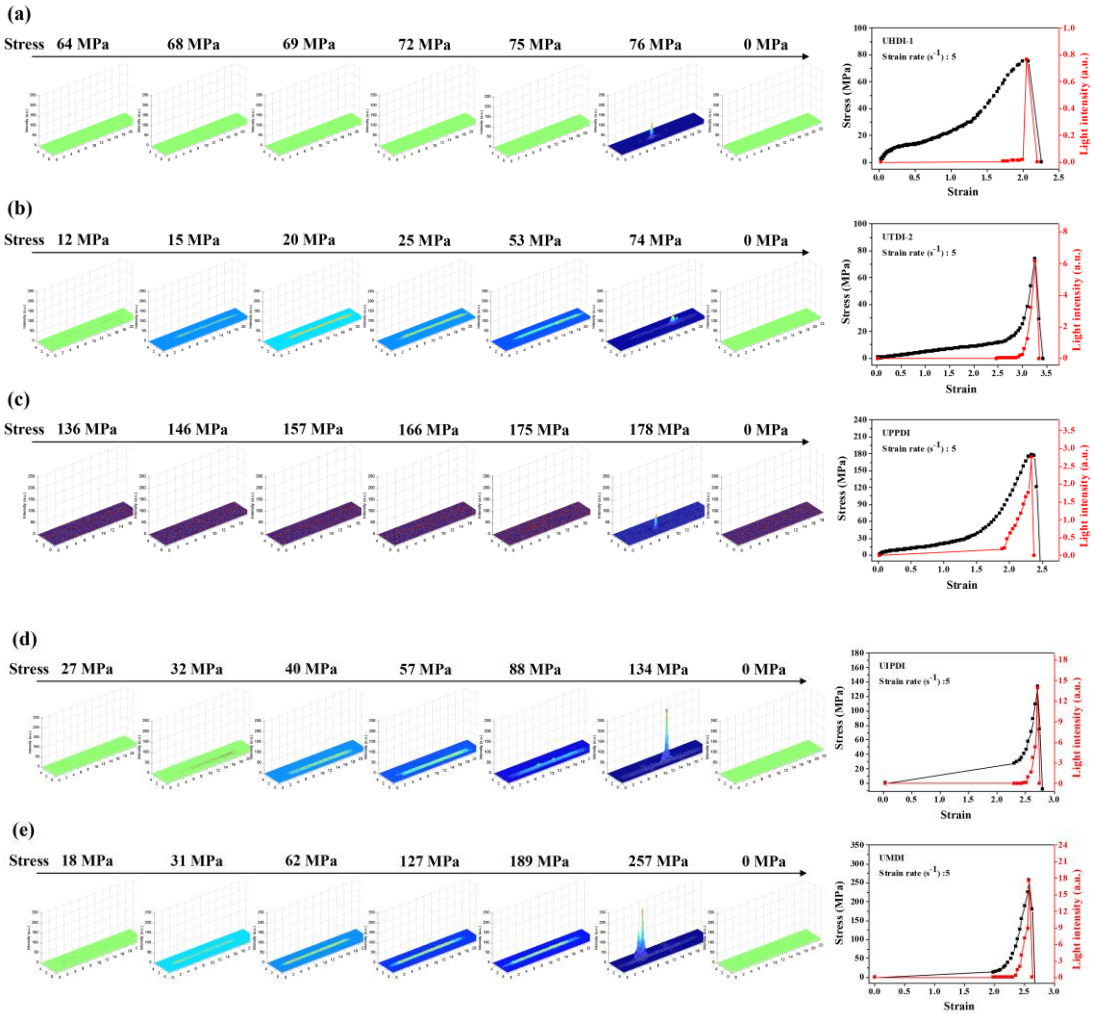


**Fig. S6** Optical images, stress and light intensity vs strain during stretching of a bulk film **UHDI-1** (a), **UTDI-2** (b), **UPPDI** (c), **UIPDI** (d) and **UMDI** (e) containing 0.2 wt % 4,7-di(thiophen-2-yl) benzo [*c*][1,2,5] thiadiazole at a strain rate of 5 $s^{-1}$.

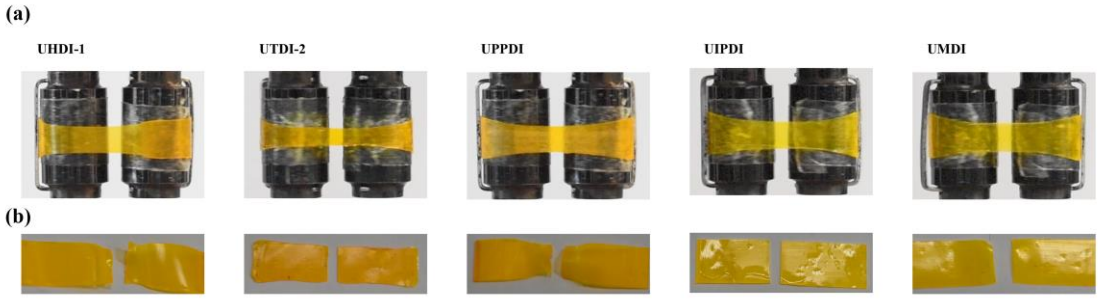


**Fig. S7** The **UHDI-1**, **UTDI-2**, **UPPDI**, **UIPDI** and **UMDI** film (a) during stretching and (b) after fracture at a strain rate of 5 $s^{-1}$.

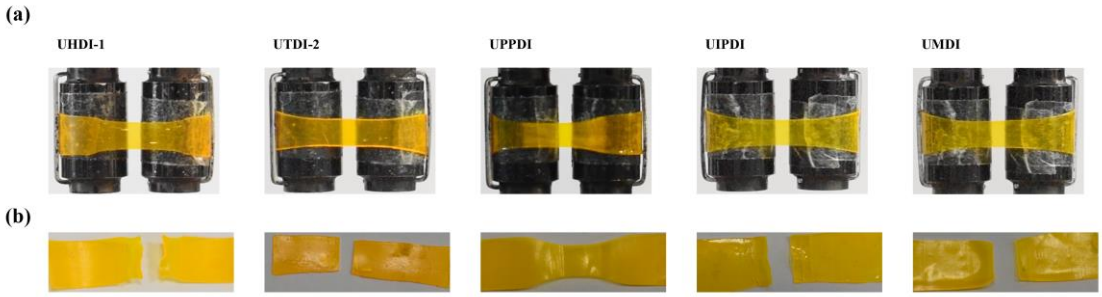


**Fig. S8** The **UHDI-1**, **UTDI-2**, **UPPDI**, **UIPDI** and **UMDI** film (a) during stretching and (b) after fracture at a strain rate of 1 $s^{-1}$.

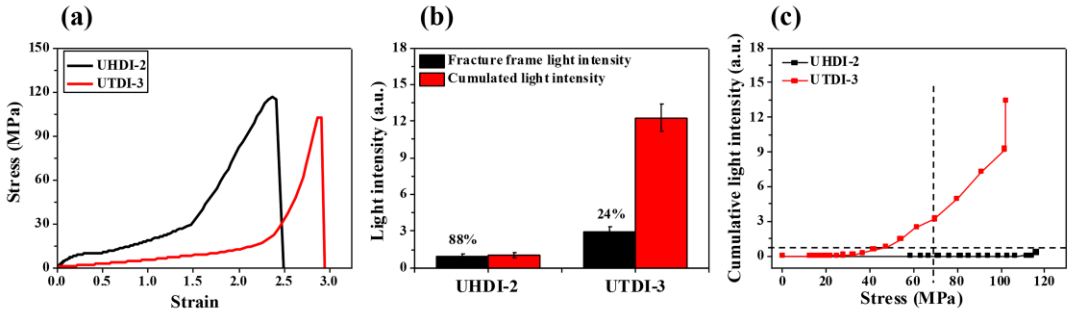


**Fig. S9** (a) Stress−strain curves, (b) fracture frame light intensity and total light intensity, and (c) cumulative light intensity *vs.* stress of mixed films of **UHDI-2** and **UTDI-3** containing 0.2 wt % 4,7-di(thiophen-2-yl) benzo[*c*][1,2,5] thiadiazole at a strain rate of 5 $s^{-1}$.

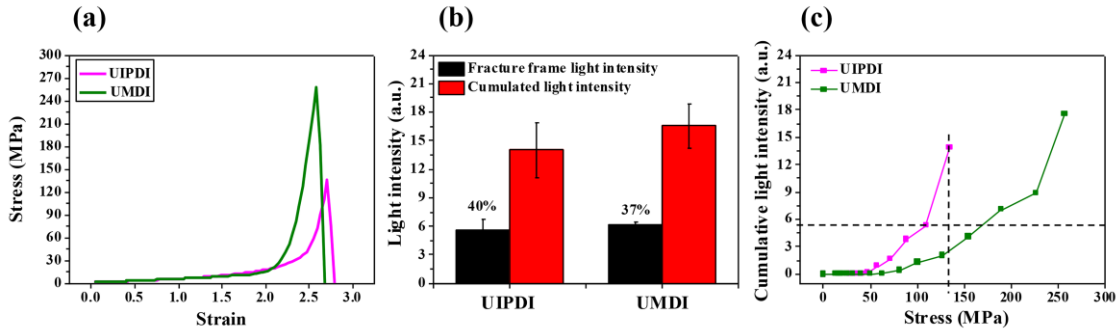


**Fig. S10** (a) Stress−strain curves, (b) light intensity of fracture frame and total light intensity, and (c) cumulative light intensity *vs.* stress of mixed films of **UIPDI** and **UMDI** containing 0.2 wt % 4,7-di(thiophen-2-yl) benzo[*c*][1,2,5] thiadiazole at a strain rate of 5 $s^{-1}$.

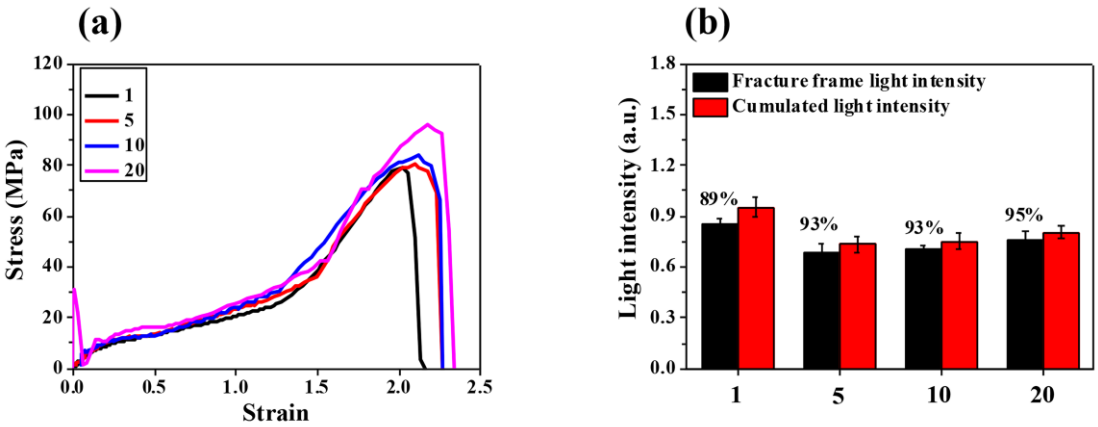


**Fig. S11** (a) Stress−strain curves and (b) light intensity of fracture frame and total light intensity emitted upon straining a film of **UHDI-1** containing 0.2 wt % 4,7-di(thiophen-2-yl) benzo [c][1,2,5] thiadiazole at different strain rates.

## References.


1. Chen, Y.; Sijbesma, R. P., *Macromolecules* **2014**, *47* (12), 3797-3805.

2. Yuan, W.; Yuan, Y.; Yang, F.; Wu, M.; Chen, Y., *Macromolecules* **2018**, *51* (21), 9019-9025.