

## Supporting Information

# Aromatic diselenide crosslinkers to enhance the reprocessability and self-healing of polyurethane thermosets

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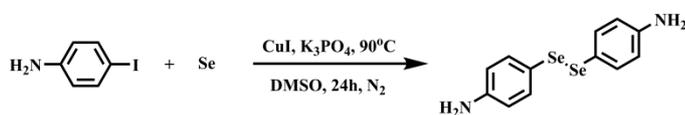
## Materials and methods

Poly(propylene glycol)s (PPG) 5 ( $M_n$  3,740) and 7 ( $M_n$  2,000) were purchased from Bayer Materials Science. Isophorone diisocyanate (IPDI, 98%), dibutyltin dilaurate (DBTDL, 95%), bis(4-aminophenyl) disulfide 1a (98%), bis(p-tolyl) disulfide 1b (98%), bis(4-methoxyphenyl) disulfide 2 (97%), 4,4'-ethylenedianiline 4 (> 95%) and tetrahydrofuran (THF) were purchased from SigmaAldrich and were used as received.

Fourier transform infrared (FTIR) spectra were registered in Nicolet 6700 spectrometer (Thermo Scientific) resolution of  $4\text{ cm}^{-1}$  and 10 scans recorded, using KBr disks compressed to  $2\text{ Ton cm}^{-2}$  for 2 min as support.  $^{13}\text{C}$  NMR spectra were registered in a Bruker AVANCE 500 MHz spectrometer. Solid NMR spectra were registered in a Bruker 400 MHz spectrometer. Dynamic mechanical analyses were performed in a Triton Tritec 2000 DMA, using a compression geometry and  $5\times 5\times 2\text{ mm}^3$  specimens. Tensile strength measurements were carried out according to Universal Instron 5569 tensile test machine Load cell of 100 N and initial distance between clamps of 30 mm and an elongation rate of  $100\text{ mm min}^{-1}$

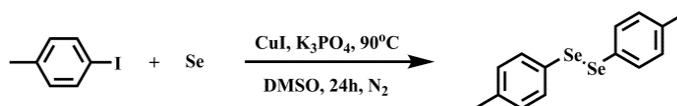
## 1. Synthesis

### 1.1 Preparation of DADPDSe



DADPDSe was synthesized according to a previous report.<sup>1</sup> To a stirred solution of Se<sup>0</sup> metal (100.0 mmol) and p-iodoaniline (20.0 mmol) in dry DMSO (200.0 mL) was added CuO nanoparticles (10.0 mol %) followed by KOH (2.0 equiv) under nitrogen atmosphere at 90 °C. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was allowed to cool, which was subjected to column chromatographic separation (Silica gel, [Hexane]/[[Ethyl acetate] = 1/1, v/v) to give pure Diselenides. 3.8g, 55% yield. The identity and purity of the product was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analysis. High-resolution mass spectrometer exact mass calculated for [M+1]<sup>+</sup> C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>Se<sub>2</sub> 344.9409, found 344.9431.

## 1.2 Preparation of DMDPDSe



DMDPDSe: 0.8g, Yield: 86%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ= 7.47 (d, J=8.4 Hz, 2H), 7.04 (d, J= 8.4 Hz, 2H), 2.30 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) δ= 139.32, 133.20, 130.51, 127.41, 22.80; <sup>77</sup>Se NMR (CDCl<sub>3</sub>, 76.28 MHz) δ= 409.6; I(KBr),ν(c<sup>-1</sup>): 2916, 1627, 1396, 802.

## 2. Model reaction

A model exchange reaction consist off dissolving 34.2 mg of 4-aminophenyl diselenide (or disulfide) in 500 mL of DMSO and brought up to the temperature of 20 °C in the NMR spectrometer after which an initial scan was recorded. Subsequently, a solution of 34.02 mg of p-tolyl diselenide in 200 mL of DMSO was added and the NMR tube was mixed briefly before inserting it into the spectrometer. The degree of product formation for the different reactions was calculated using the following fraction of the integrals of a and b in the NMR (Equation (1))

$$Y = \frac{I(b)}{I(a)+I(b)} \quad (1)$$

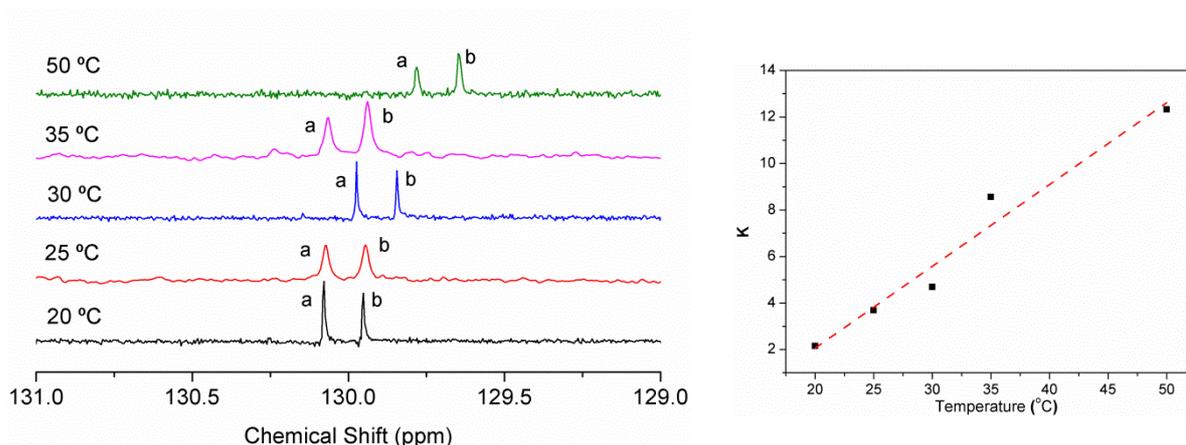
Similarly, the equilibrium constant at different temperatures was calculated using the yield in the equilibrium, according to equation (2):

$$K = \frac{Y^2}{(1-0.5Y)^2} \quad (2)$$

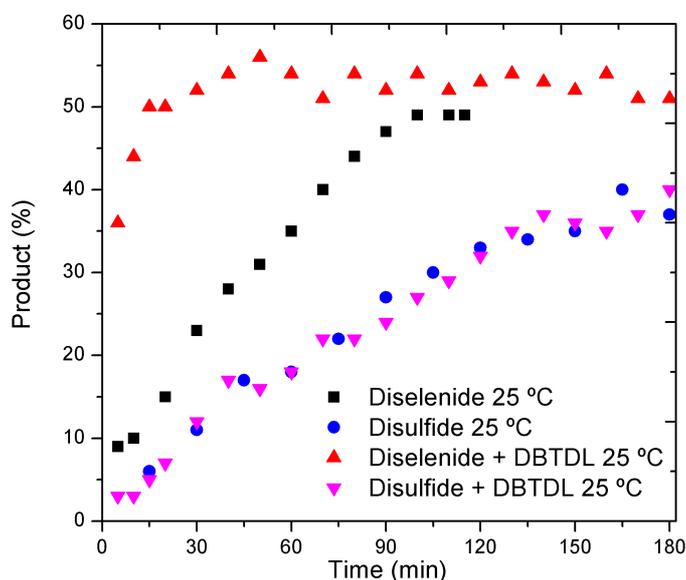
**Table S1** Detailed description of the exchange reactions studied by <sup>13</sup>C NMR

Reaction	R	X	Y	Solvent	Time (h)	Temperature (°C)
i	1:1	Se	Se	DMSO	2	20
ii	1:1	Se	Se	DMSO	2	25
iii	1:1	Se	Se	DMSO	2	30
(iv)	1:1	Se	Se	DMSO	2	35
(v)	1:1	Se	Se	DMSO	2	50
(vi)	1:1	S	S	DMSO	2	25
(vii)*	1:1	Se	Se	DMSO	2	25
(viii)*	1:1	S	S	DMSO	2	25

\* In the case of reactions (vii) and (viii), 100 ppm of dibutyltin dilaureate (DBTDL) were added to the mixture.



**Figure S1.** <sup>13</sup>C NMR spectra of the exchange reaction of 4-aminophenyl diselenide with p-tolyl diselenide and 4-aminophenyl disulfide with p-tolyl disulfide (delay time of 20 s) (left) and equilibrium constant vs. temperature dependence calculated using Equation (2).



**Figure S2.** Conversion vs. time plots in the absence and in the presence of 100 ppm of dibutyltin dilaurate (DBTDL) for the corresponding model reactions of diselenide and disulfide at 25 °C.

### 3. Healable polyurethane synthesis

#### 3.1 Synthesis of tris-isocyanate-terminated prepolymer 4

A mixture of PPG (3740g/mol) (30 g, 8.02 mmol) and IPDI (5.35 g, 24 mmol) were fed into a 500mL glass reactor equipped with mechanical stirrer and a vacuum inlet. The mixture was degassed by stirring under vacuum while heating at 65 °C for 30 min. Then DBTDL (50 ppm) was added and the mixture was further stirred under vacuum at 65 °C for 30 minutes. The reaction was monitored by FTIR spectroscopy (Figure S1). The resulting tris-isocyanate terminated prepolymer was obtained in the form of a colorless liquid and stored in a tightly closed glass bottle. Yield: 31 g, 88%.

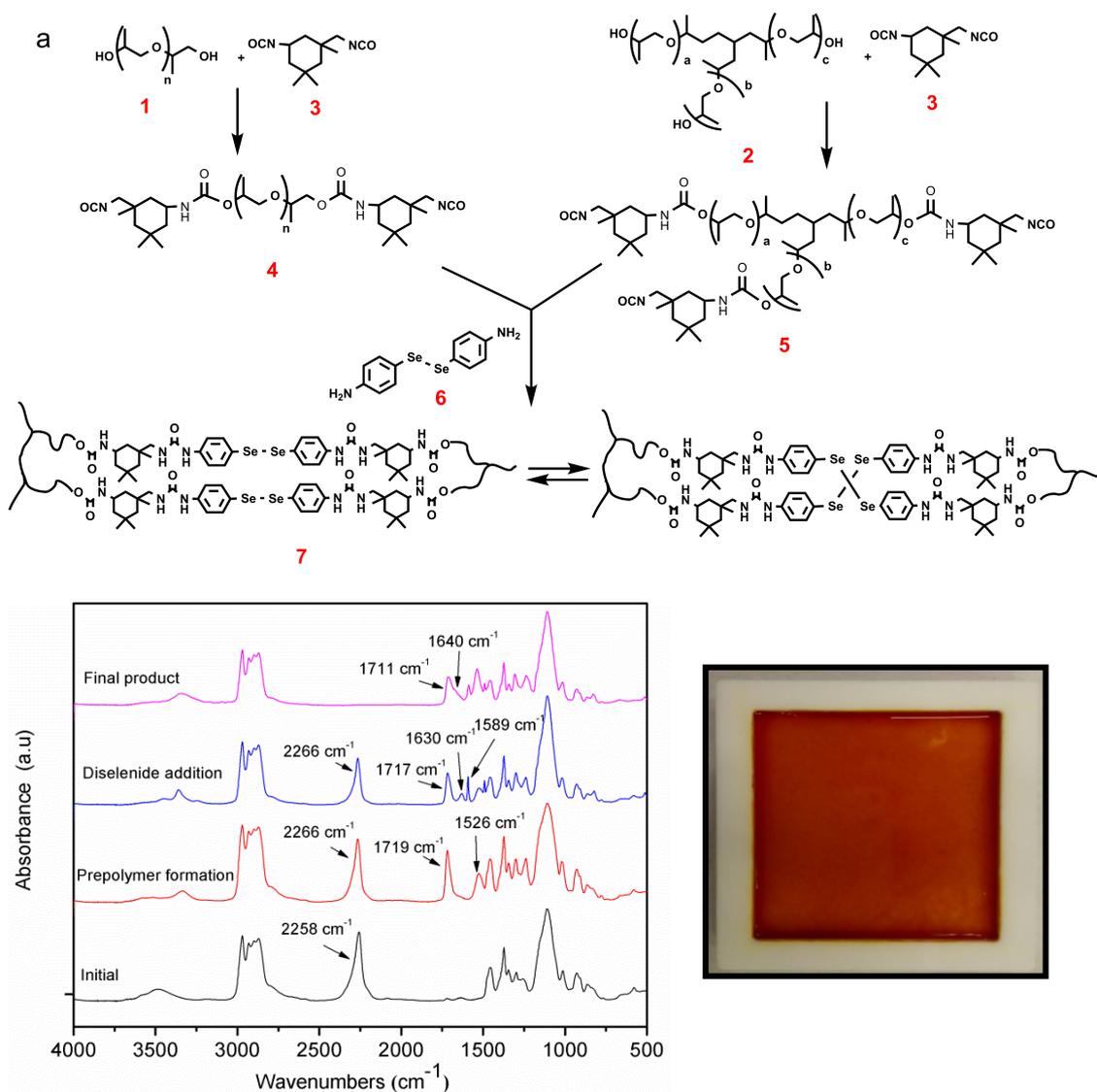
#### 3.2 Synthesis of bis-isocyanate-terminated prepolymer 5

A mixture of PPG (2000g/mol)(30 g, 15 mmol) and IPDI (6.66 g, 30 mmol) were fed into a 500mL glass reactor equipped with mechanical stirrer and a vacuum inlet. The mixture was degassed by stirring under vacuum while heating at 60 °C for 30 min. Then DBTDL (50 ppm) was added and the mixture was further stirred under vacuum at 60 °C for 60 minutes. The

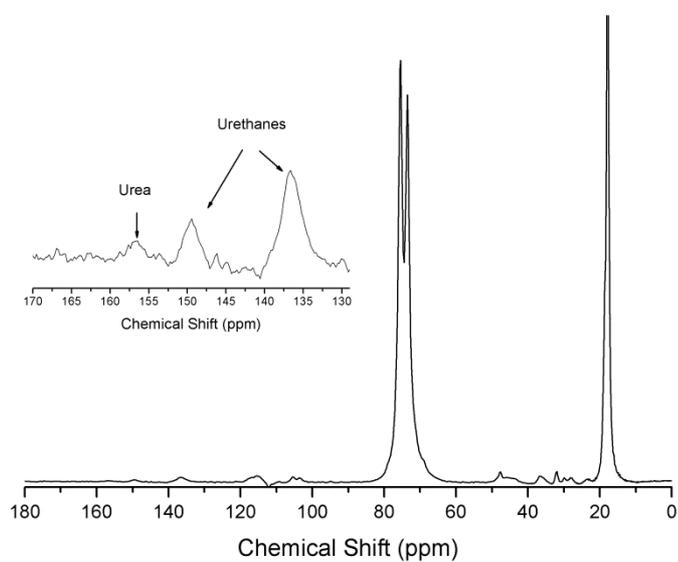
reaction was monitored by FTIR spectroscopy (Figure S1). The resulting bis-isocyanate terminated prepolymer was obtained in the form of a colourless liquid and stored in a tightly closed glass bottle. Yield: 34 g, 93%.

### 3.3 Synthesis of self-healing poly(urea-urethane) elastomer based on diselenide

4 (4.00 g) and 5 (2.22g) were mixed in a 250 mL glass reactor. Then, a solution of DAPDSe (0.18 g, 1.82 mmol) in THF (3 mL) was added. The mixture was degassed under vacuum for 15 minutes and the mixture was placed on to an open mould. The curing was allowed to proceed for 24 h at 60 °C and was monitored by FTIR spectroscopy.

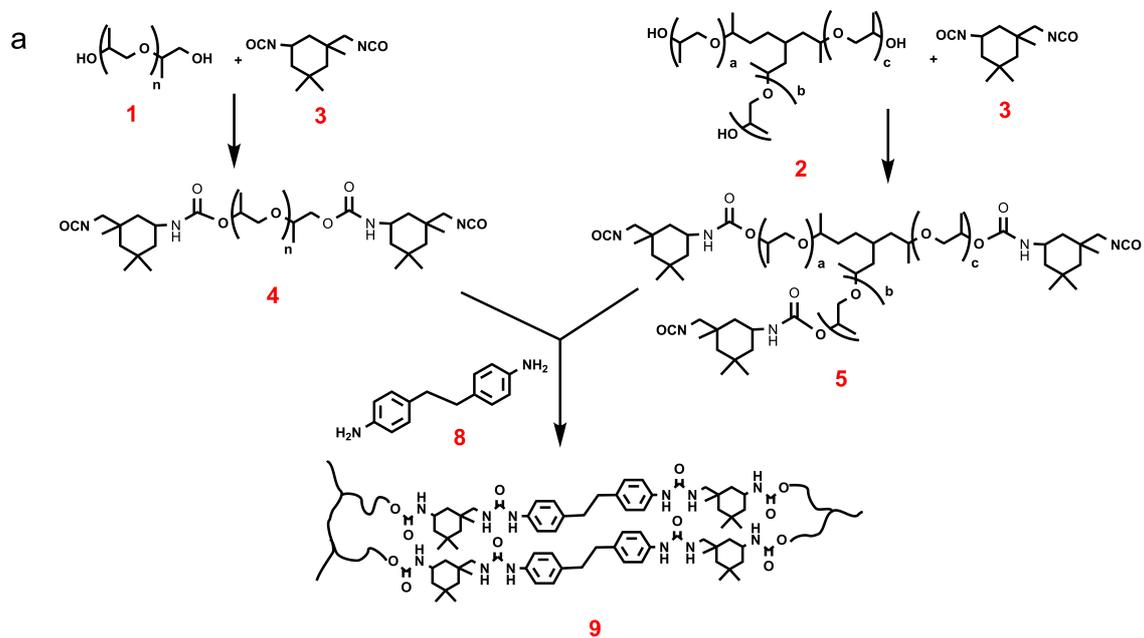


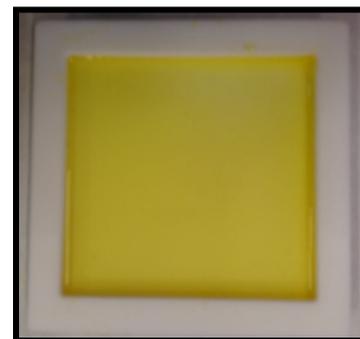
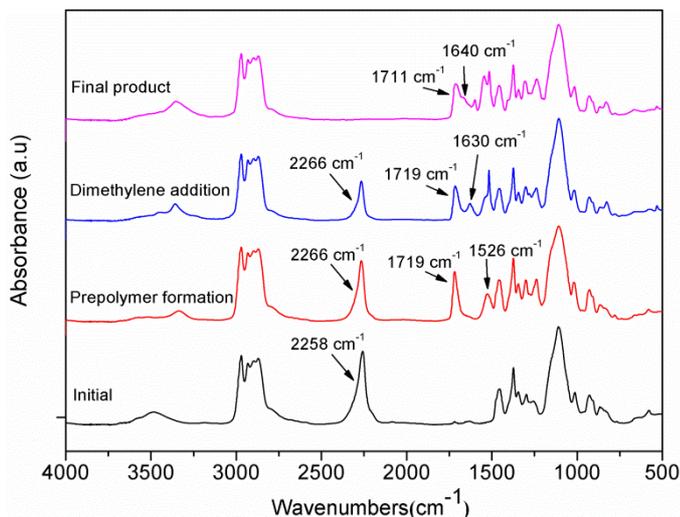
**Figure S3.** FTIR spectra of reaction of PPG4000 and PPG2000 (1:1) and IPDI at 65 °C at  $t = 0$  (black trace) and  $t = 60$  min. (red trace, prepolymer formation), where the appearance of new bands corresponding to the carbonyl group of urethane moiety at 1719  $\text{cm}^{-1}$  and amide II at 1526  $\text{cm}^{-1}$  can be observed. Moreover, a decrease and displacement of the NCO stretching band from 2258 to 2266  $\text{cm}^{-1}$  can be observed, which was used as criteria to establish that the reaction was finished. The mixture was cured by the addition of diselenide amine crosslinker in a mould at 60 °C. Spectra were recorded at  $t = 0$  min (blue trace, diselenide addition) and  $t = 24$  h (pink trace, final). The NCO stretching band at 2266  $\text{cm}^{-1}$  completely disappeared and a new band corresponding to the urea appeared at 1640  $\text{cm}^{-1}$  in the form of a shoulder. (The spectra have been shifted for clarity).



**Figure S4.** Solid state  $^{13}\text{C}$  NMR spectra of the obtained diselenide based polyurethane. The peak at 157 ppm as well as the peaks at 149 and 136 ppm confirms the urea and urethane formation respectively.

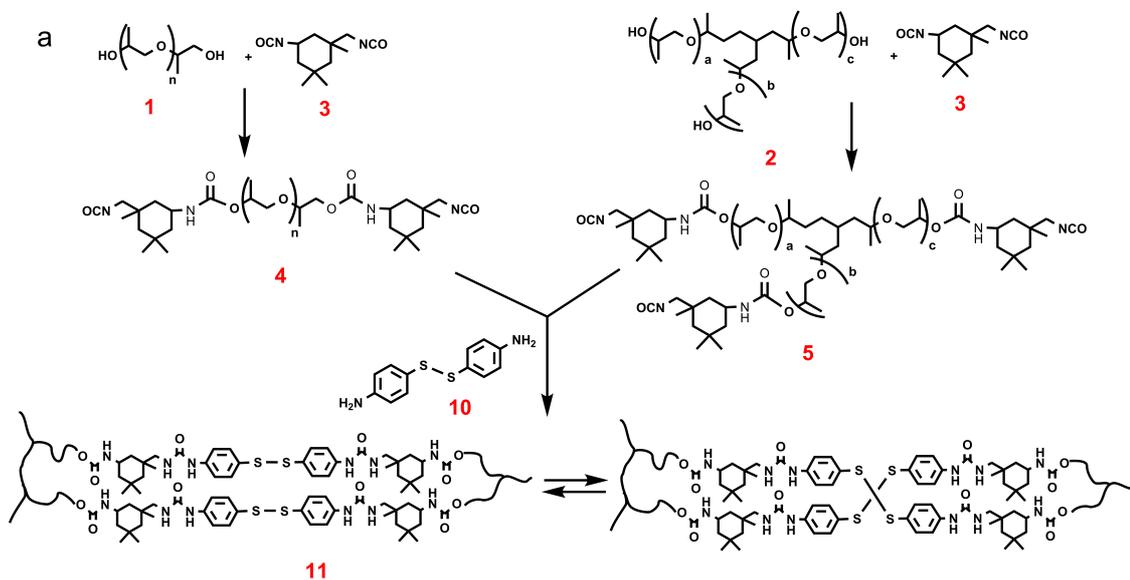
### 3.4 Synthesis of self-healing poly(urea-urethane) elastomers based on aromatic dimethylene.

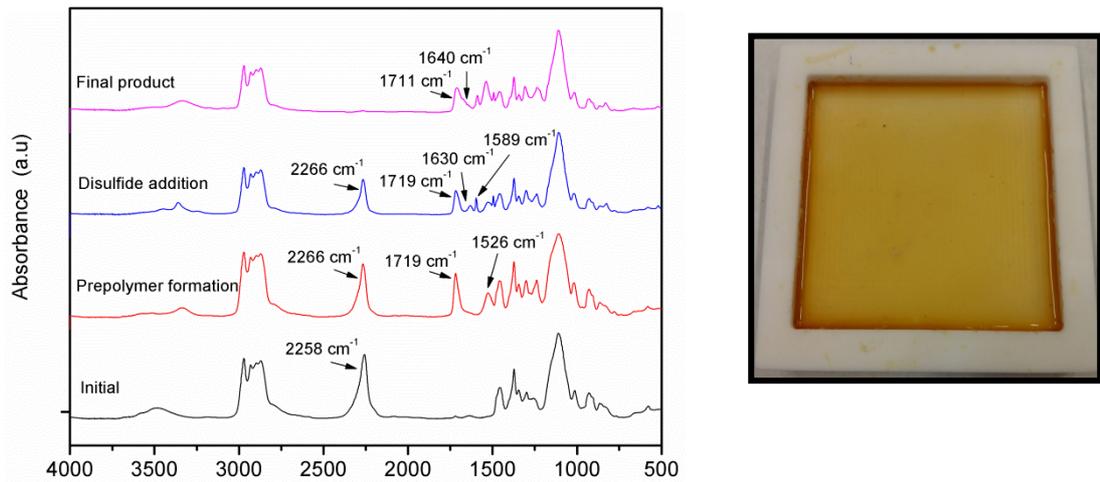




**Figure S5.** FTIR spectra of reaction of PPG4000 and PPG2000 (1:1) and IPDI at 65 °C at  $t = 0$  (black trace) and  $t = 60$  min. (red trace, prepolymer formation), where the appearance of new bands corresponding to the carbonyl group of urethane moiety at  $1719\text{ cm}^{-1}$  and amide II at  $1524\text{ cm}^{-1}$  can be observed. Moreover, a decrease and displacement of the NCO stretching band from  $2258$  to  $2266\text{ cm}^{-1}$  can be observed, which was used as criteria to establish that the reaction was finished. The mixture was cured by the addition of aromatic dimethylene crosslinker in a mould at  $60\text{ }^{\circ}\text{C}$  at  $0$  min (blue trace, dimethylene addition) and  $t = 24\text{ h}$  (pink trace, final). The NCO stretching band at  $2266\text{ cm}^{-1}$  completely disappeared and a new band corresponding to the urea appeared at  $1640\text{ cm}^{-1}$  in the form of a shoulder. (The spectra have been shifted for clarity).

### 3.5 Synthesis of self-healing poly(urea-urethane) elastomer **6c**

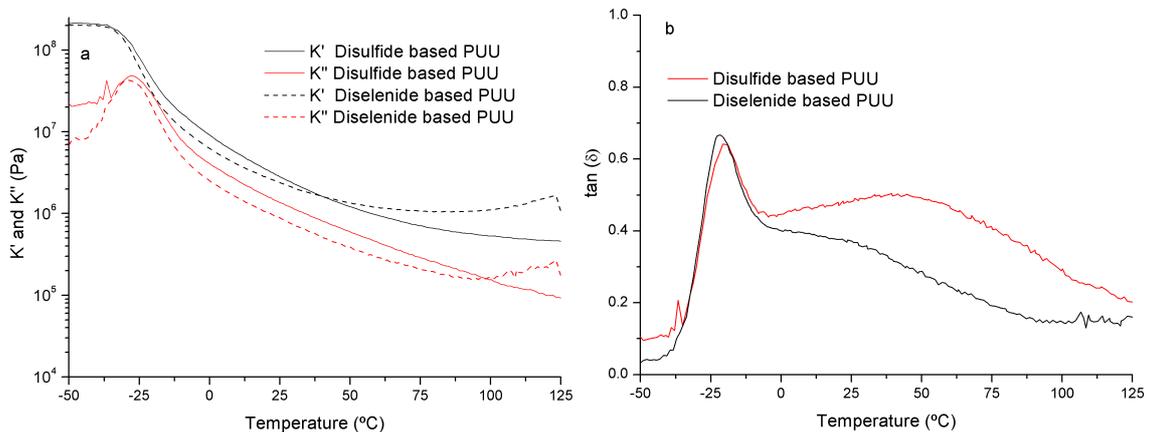




**Figure S6.** FTIR spectra of reaction of PPG4000 and PPG2000 (1:1) and IPDI at 65 °C at  $t = 0$  (black trace) and  $t = 60$  min. (red trace, prepolymer formation), where the appearance of new bands corresponding to the carbonyl group of urethane moiety at  $1719\text{ cm}^{-1}$  and amide II at  $1524\text{ cm}^{-1}$  can be observed. Moreover, a decrease and displacement of the NCO stretching band from  $2258$  to  $2266\text{ cm}^{-1}$  can be observed, which was used as criteria to establish that the reaction was finished. The mixture was cured by the addition of aromatic disulfide crosslinker in a mould at  $60\text{ °C}$  at  $0\text{ min}$  (blue trace, dimethylene addition) and  $t = 24\text{ h}$  (pink trace, final). The NCO stretching band at  $2266\text{ cm}^{-1}$  completely disappeared and a new band corresponding to the urea appeared at  $1640\text{ cm}^{-1}$  in the form of a shoulder. (The spectra have been shifted for clarity).

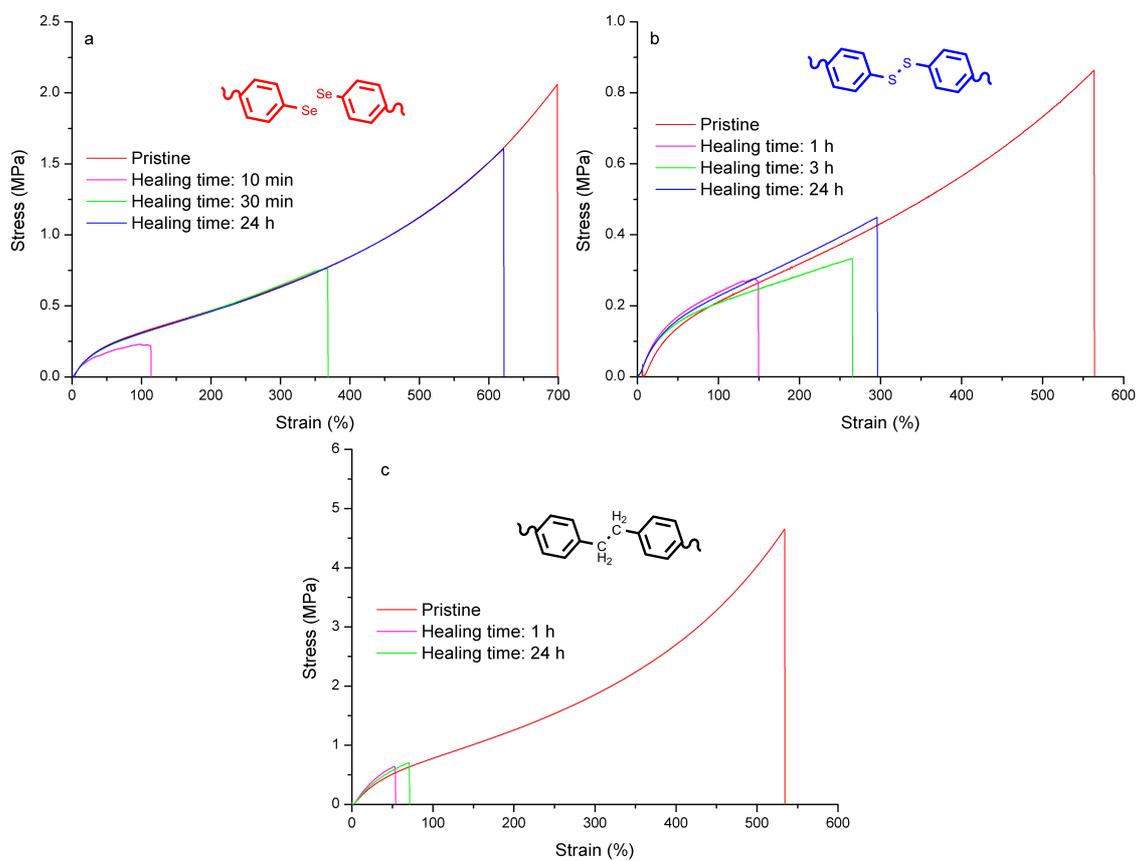
#### 4. Thermal and mechanical properties of the synthesized materials

##### 4.1 Thermal properties



**Figure S7.** DMA plots for the synthesized disulfide and diselenide polymers. As observed in the  $\tan(\delta)$  vs. temperature plot, the glass transition temperature of the soft segment remains almost invariable, regardless the nature of the aromatic crosslinker. However, the  $T_g$  of the hard segment is around  $20\text{ °C}$  lower for the diselenide with respect to the disulfide based polyurethanes.

## 4.2 Mechanical properties of pristine and healed materials



**Figure S8.** Representative stress-strain graphs for aromatic diselenide (a), disulfide (b) and dimethylene (c) based systems. The healed specimens were tested after being cut in two parts, put in close contact and kept for different healing times.