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Electronic Supplementary Information

A Robust and Self-healing Elastomer Achieved by Thio-8diketone-Cu(II) Coordination and H-Bonding Dual Crosslinked System

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Methods

Nuclear Magnetic Resonance spectra (NMR) were recorded on a Bruker DRX 400 NMR spectrometer at room temperature with use of the deuterated solvent and the residual solvent was used as the internal reference (DMSO- d_6 , δ 2.50 ppm for ¹H NMR, δ 39.9 ppm for ¹³C NMR).

Isothermal Titration Calorimetry (ITC). All titrations were performed using a MicroCal ITC200 isothermal titration calorimeter at 298.15 K. The solutions were prepared in dry MeOH using vacuum-dried hosts and guests. Twenty aliquots (2 μ L each) of inorganic salt in dry MeOH were added into the ligand solution with 150 s injection interval to measure the heat of complexation. Blank titrations in dry MeOH were performed and subtracted from the corresponding titrations to remove the effect of dilution. The titration curve thus obtained was analyzed using ORIGIN software, giving parameters concerning the binding affinity (*K*) and thermodynamic parameters (ΔH and ΔS) of different titrations.

Gel Permeation Chromatography (GPC) was performed at a flow rate of 1.0 mL/min with tetrahydrofuran (THF) as the elution moving phase on a PL-GPC 120 system equipped with a refractive index (RI) detector, and narrowly dispersed polystyrene species were employed as the molecular weight standard.

UV-vis absorption spectra were measured in SHIMADZU UV3600 spectrophotometer, using MeOH as the solvent.

Infrared radiation spectra (IR) were recorded with Bruker Tensor II infrared spectrometer (range: 3900-500 cm⁻¹).

The *in situ* **X-ray photoelectron spectroscopy (XPS)** analysis was performed on a PHI 5000 VersaProbe system, using monochromatic Al K α radiation (1486.6 eV). The binding energies were corrected by setting the graphite carbon C 1s signal of 284.6 eV as reference.

Transmission Electron Microscope (TEM) photography was recorded with FEI Tecnai GF20 transmission electron microscopy.

All the **mechanical tensile-stress experiments** were performed using an Instron 34SC-1 Microtester. For mechanical tensile-stress and self-healing test, sample size of 10 mm length × 2 mm width × 1 mm height, gauge length of 3 mm, and strain rate of 20 mm×min⁻¹ were adopted. All samples were tested at ambient conditions.

Rheology experiments were tested on Discovery HR-2 TA rheometer. Frequency-dependent moduli of the samples were tested at 100, 80, 60, 40, 20 °C. Master curves of the dynamic moduli of PU-SO-Cu, PU-SO, PU-BD and PU-BD-Cu were scaled by WLF equation:

$$\log(a_{T}) = \frac{-C_{1}(T-T_{r})}{C_{2} + (T-T_{r})}$$

Where a_T is the horizontal shift factor, and T_r is the reference temperature.

Temperature-dependent modulus was tested from 38 °C to 100 °C, with the frequency of 15 Hz. Wide-angle X-ray diffraction pattern (WXRD) were tested on a BRUKER D8 ADVANCE diffractometer with a Cu K α X-ray source (λ = 1.540598 Å).

Scanning Electron Microscope (SEM) was used to observe the morphologies of samples by a scan electron microscopy S-4800 equipped with a camera operated at 20 kV.

Calculation of the hysteresis, dissipation and fracture energies. The hysteresis was measured by subjecting a sample containing no crack to load and unload. And the hysteresis was defined by W_D/W , where W was the area under the stress-stretch curve measured on loading, and W_D was the area between the loading and unloading curves.

The dissipation was defined by $W_{D/}W_{D-0}$, where W_{D-0} was the area between the loading and unloading curves measured in the first cycle.

The fracture tests were conducted using the classical single-edge notch test on the Instron 34SC-1. A notch of 2 mm in length was made in the middle of a rectangular specimen of about 0.5 mm in thickness and 7 mm in width. The specimen was fixed in two clamps with a pre-set distance of 5 mm. Then, the specimen was subjected to uniaxial tension with a strain rate of 20 mm/min. The fracture energy (G_c) was calculated by a method developed by Greensmith¹ which in essence introduces an empirical correction factor of:

$$G_{\rm c} = \frac{6Wc}{\sqrt{\lambda_{\rm c}}}$$

where c is the notch length; W is the strain energy calculated by integration of the stress-strain curve of an unnotched specimen until λ_c ; the unnotched specimen underwent a tension process with the same strain rate as the notched sample.

For **self-healing tests**, all the samples were cut into two completely separate pieces with a razor blade. The two half films were gently brought back into contact with a distance about ~ 40 μ m and then healed at different temperatures for 3 hours. The healing efficiency was calculated by the strain at break and divided by that of the uncut samples under heating at 80 °C for 3 hours.

The **X-ray absorption fine structure (XAFS)** measurements were performed on the BL14W1 beamline at Shanghai Synchrotron Radiation Facility (SSRF) under the fluorescence mode. The energies were calibrated accordingly to the absorption edge of pure Cu and Mn foils. Athena and Artemis codes were used to extract the data and fit the profiles. For the X-ray absorption near edge structure (XANES) part, the experimental absorption coefficients as a function of energies $\mu(E)$ were processed by background subtraction and normalization procedures and reported as "normalized absorption" with E₀ = 8979.0 eV for all the tested samples and Cu foil standard. Then all the EXAFS and XANES data were analyzed by the Demeter software².

The *in-situ* **small-angle x-ray scattering (SAXS)** measurements were performed on BL16B1 beamline at Shanghai Synchrotron Radiation Facility (SSRF). The incident x-ray beam with an energy of 10 keV was used, and it was normal to the sample film so that the SAXS was in transmission geometry. A Pilatus 2m x-ray detector was used, with a sample-to-detector distance of 1900 mm. The 2D images were then reduced into scattering intensity (I) as a function of scattering vector ($q = 4\pi \sin\theta/\lambda$, where θ is half of the scattering angle and λ is x-ray wavelength.) using the software equipped at the beamline. *In-situ* stretching-SAXS measurements were based on a stretch station which can be controlled by wireless. SAXS data were recorded at different strain.

Capacitance of the pressure sensor under pressure was measured using an LCR meter (4284A or E4980AL, Keysight). A high-precision mechanical system (AG-X, Shimazu) was used to control the pressure applied to the sensor. For cyclic pressure applications, pressure was applied for 2 sec and released for 2 sec, repeatedly. A friction apparatus (FPR2200, RHESCA CO., LTD) was used for the friction test. In order to control the friction applied to the sensor surface, a spherical polyurethane of 3 mm diameter was used, and surface of the sensor was rubbed with a speed of 20 mm/s.

Conductivity of the strain sensor during stretching

The prepared electrode was firstly held on the Instron 5944 Microtester. The initial distance between the clamps was about 15 mm. Each clamp held a copper wire which was connected with the AgNWs on the strain sensor. In order to reduce the contact resistance between the wire and the AgNWs, liquid metal (Gallium-indium eutectic) was injected at the interfacial. The stretching speed was set at 2 mm/min. The data of stain and resistance were simultaneously collected and the gauge factor (G_F) was calculated by the following equation:

$$G_F = (R - R_0) / R_0 \varepsilon.$$

where R_0 was the initial resistance; R was the measured resistance; ε was the strain.

The resistance changes of the strain sensor were tested on a Keithley Model 6514 system electrometer. Zero check should always be enabled before making function or connection changes. The data collection depends on the program by LabVIEW.

Synthesis of the SO ligand



Molecular weight according to GPC: $M_w = 173 \text{ kDa}$ and $M_n = 43 \text{ kDa}$ ($\oplus = 4.07$). ¹H NMR (400 MHz, DMSO- d_6): δ 10.10 (s, 1H), 10.00 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 7.7 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 4.80 (t, J = 5.4 Hz, 2H), 4.42-4.37 (m, 1H), 3.77 (s, 2H), 3.60-3.55 (m, 4H). ¹³C NMR (100 MHz, DMSO- d_6): δ 195.9, 166.4, 139.4, 129.2, 123.9, 119.6, 59.5, 59.1, 53.1.

Synthesis of the control samples

PU-SO & PU-SO-Cu

IPDI (isophorine diisocyanate) and PTMG (polytetramethylene glycol, M_n =1000g/mol) were dried under vacuum at 70°C overnight. Subsequently, IPDI (4 mmol) and catalytic amount of dibutyltin dilaurate (DBTDL) were added into three-necked flask equipped with mechanical stirrer under nitrogen, followed by adding PTMG (2 mmol) into the prepolymer and stirred under 80°C for 5 h. Then, 1, 4-butanediol (BDO, 1 mmol) and SO (1mmol) were added into the prerpolymer. The mixture was stirred at 80°C for 5 h and the reactant was poured into a poly tetrafluoroethylene (PTFE) plate. The plate was put in an oven at 80°C for 24 h to make the reaction fully complete, then the PU-SO film was prepared.

PU-SO (2.0 g) and $CuCl_2 \cdot 2H_2O$ (23 mg, Cu:SO=1:3) were dissolved in 20 mL DMF. Then the reaction was stirred at 80°C for 8 h and then concentrated. The concentrated solution was poured into a PTFE plate. The plate was dried at 80 °C for 24 h. The PU-SO-Cu film was then prepared.



PU-BD & PU-BD-Cu

IPDI and PTMG were dried under vacuum at 70°C overnight. Subsequently, IPDI (4 mmol) and catalytic amount of dibutyltin dilaurate (DBTDL) were added into three-necked flask equipped with mechanical stirrer under nitrogen, followed by adding PTMG (2 mmol) into the prepolymer and stirred under 80°C for 5 h. Then, BDO (2 mmol) was added into the prepolymer. The mixture was stirred at 80°C for 5 h and the reactant was poured into a poly tetrafluoroethylene (PTFE) plate. The plate was put in an oven at 80°C for 24 h to make the reaction more complete, then the PU-BD film was prepared.

PU-BD (2g) and $CuCl_2 \cdot 2H_2O$ (23mg) were dissolved in 20 mL DMF. Then the reaction was stirred at 80°C for 8 h and then concentrated. The concentrated solution was poured into a PTFE plate. The plate was dried at 80 °C for 24 h. The PU-BD-Cu film was then prepared.





Fig. S1 ¹H and ¹³C NMR spectra of SO ligand (400 M for ¹H NMR and 100 M for ¹³C NMR, DMSO- d_6 , R. T.).



Fig. S2 FT-IR spectra of the samples PU-BD, PU-SO and PU-SO-Cu.



Fig. S3 ¹H NMR spectra of PU-SO (400 M, DMSO- d_6 , R. T.).



Fig. S4 WXRD spectra of the samples PU-SO and PU-SO-Cu.

Table S1 Thermodynamic Parameters for the Coordination of Cations Binding to Ligands Determined by ITC $^{\rm a}$

Host (in cell)	Guest (in syringe)	К	∆H (kcal/mol)	ΔS (cal/(mol*K))
SO ligand (0.3 mM)	CuCl2 (3 mM)	5.91×10 ⁴	-5.7 ± 0.3	2.67

[a] All titration experiments were performed in MeOH at 298 K.

Table S2 Mechanical performances of the samples PU-SO-Cu, PU-SO, PU-BD and PU-BD-Cu ^a

Sample	Strength	Elongation	Young's modulus	Toughness
PU-SO-Cu	4.35±0.16 MPa	3410±190 %	1.92±0.22 MPa	81±6.5 MJ/m ³
PU-SO	0.45±0.04 MPa	3280±220 %	1.31±0.17 MPa	11±0.9 MJ/m ³
PU-BD	0.08±0.01 MPa ^b	>2500 %	0.49±0.06 MPa	0.5±0.1 MJ/m ³
PU-BD-Cu	0.04±0.01 MPa ^b	>2500 %	0.28±0.04 MPa	0.4±0.1 MJ/m ³

[a] All the mechanical tests were measured at room temperature, with a tensile rate of 20 mm/min. [b] The strength was recorded at the yielding point.



Fig. S5 Cyclic tensile test of the PU-SO-Cu at a fixed stretch rate of 5 mm/min, the sample was loaded to 400% strain initially and then unloaded to the original length (cycle 1). After that stretched to a higher strain (600%) immediately and released the load which marked cycle 2. The cyclic test was repeated as the similar procedure except gradually increased the strain until 1200%.



Fig. S6 Fracture energy test of PU-SO-Cu, at a stretch rate of 20 mm/min. Black line represents the tensile test of the original sample, red line represents the notched sample.



Fig. S7 Graphic comparison of fracture toughness for some self-healing elastomers and hydrogels reported in the previous literatures³⁻¹².



Fig. S8 Normalized stress-relaxation curves of PU-SO and PU-SO-Cu measured at 25 $^\circ$ C.



Fig. S9 (a) The ITC titration data of the SO ligand with $MnCl_2$ in anhydrous MeOH at 25 °C. (b) Typical stress–strain curve of PU-SO-Mn, with tensile rate of 20 mm/min. (c) Recovery and cyclic loading of the film PU-SO-Cu. The samples were loaded (600% strain), unloaded, and immediately reloaded ten times (tensile rate: 20 mm/min), and then the samples were allowed to rest for 1 hour at 25 °C after releasing of the strain and stress again.

Table S3 Comparison of binding ability and mechanical properties between PU-SO-metals

Sample	Binding ability K	Young's modulus	Stress at break	Toughness
PU-SO-Mn	1.65*10 ⁴	1.39 MPa	3.57 MPa	46 MJ/m ³
PU-SO-Cu	5.91*10 ⁴	1.92 MPa	4.35 MPa	81 MJ/m ³
PU-SO	-	1.31 MPa	0.45 MPa	11 MJ/m ³



Fig. S10 Self-healing efficiency of PU-SO-Cu with different healing temperature for 3 hours, in terms of strain at break.



Fig. S11 Temperature-dependent loss modulus of PU-SO-Cu, with ω =15 Hz.



Fig. S12 Comparison of the strain, stress and healing temperature of the PU-SO-Cu with recently reported self-healing polymers^{9, 13-23}.



Fig. S13 1D scattering profiles of PU-SO-Cu integrated in different directions (horizonal and vertical) under different strains, from the 2D SAXS patterns.



Fig. S14 Experiment data and fitting data of the relative resistance changes of the sensor under different strains.

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