Supporting Information

Self-healable Polyurethane Elastomers: Enabled by the cerium salt

Zhe Wang [a], Xiao-Bin Gong [a], Jing-Chuan Xu [a], Jing-Wei Wang [a], Ya-Nan Li [a], Xin Ge [a], Rui-Guang Xinga*[a], Gao-Fei Pan*[a]

School of Materials and Metallurgy, Inner Mongolia University of Science and Technology, 7# Arerding Street, Kun District, Baotou 014010, China.

Corresponding Author

Email: *2019962@imust.edu.cn (G.-F. Pan), *xingrg06@imust.cn (R.-G. Xing)

1 Measurements

1.1 Structural analysis

^{1}HNMR and ^{13}CNMR spectra were recorded at 400 MHz using $CDCl_3$ or $(CD_3)_2SO$ as solvent. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), $(CD_3)_2SO$ (δ 2.50 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br. s = broad singlet.

FTIR measurements were used to characterize the compound and polymer structure. Fourier transform infrared spectra (FT-IR) and attenuated total reflectance Fourier transform infrared spectrometry (ATR-FTIR) were obtained from a Bruker Tensor 27 FT-IR spectrometer in the wavenumber range from 4000 to 400 cm^{-1}. Infrared (FT-IR) data were recorded as films on potassium bromide plates. In the ATR-FTIR test, data with the ".CSV" format was obtained, and then "Origin 8" software was used to fit the ATR-FTIR curves.

Gel permeation chromatography (GPC, Agilent LC1200, USA) at 25 ºC equipped with a refractive index detector using THF as a mobile phase was employed for evaluation of molecular weight and poly dispersion index (PDI).

Thermal analysis: thermal stability was performed on a thermogravimetric analysis (TG) 209F1 apparatus (NETZSCH, Germany) under nitrogen flow of 30 mL/min. Samples were examined from 50 to 700 °C at a heating rate of 10 ºC / min.

Dynamic mechanical analyzer (DMA): was carried out on a TA Q800 DMA apparatus (TA Instruments, USA) under an amplitude of 10 μm and a frequency of 1 Hz. The temperature was ranged from -80 to 60 °C at a rate of 5 °C/min. Rectangular specimens (15 mm (L) * 6 mm (W) * 1 mm (T)) were mounted on the fixture and the measurements were carried out in tension mode. The glass transition temperature (Tg) was calculated from the maximum value of tan δ (E''/E')

TGA experiments were performed on a Mettler 851e instrumentat at a heating rate of 10 ∘C·min≡ 1 from 50 to 800 ∘C under nitrogen atmosphere.

XRD measurements were completed on Bruker D8 Advance using Cu Kα radiation (λ = 0.1541 nm).

XPS spectra were obtained on a PHI QUANTERA II (ULPAC-PHI) X-ray photoelectron spectrometer.

SEM measurements were carried out with a QUANTA 250 FEG.

The mechanical properties of all the samples were tested using a universal testing machine (Instron 1121) at a strain rate of 100 mm min^{-1}. First, the prepared PU films were cut into dumbbell-like shapes with dimensions of 35 mm × 2 mm × 0.5 mm for the tensile and self-healing tests. The result for each sample corresponded to the average of five test results.

Cyclic tensile tests: The cyclic tensile tests were performed using the same instrument with a 250 N load cell. The samples were loaded, unloaded, and immediately reloaded 10 times, both loading and unloading were performed with a constant extension rate of 10 mm/min at room temperature. In each cycle, the sample was stretched to a strain of 200%. After 10 cycles, the samples were allowed to relax at room temperature for 10 min before next loading cycle.

Healing Efficiency %: The ultimate tensile strengths of the samples before and after repair were compared to evaluate the repair performance of the TPU. In the repair experiment, the sample was cut through the middle by using a razor and later spliced. The spliced sample was maintained at room temperature for different durations to induce self-healing. After the sample was healed, it was subjected to a tensile test, and the ultimate tensile strength (σ) was recorded. The self-healing efficiency was defined as follows: Healing Efficiency % = σ of healing sample / σ of original sample × 100%.

Thermal conductivity λ： The thermal conductivity λ is termed as: $\lambda = \alpha\, C_p\, \rho$, where α is the thermal diffusivity, C_p is the specific heat and ρ is the density of the composites. The α of materials were measured by TA instrument DXF-900, which voltage and testing temperature were set to be 500–550 V and 50 ◦C, respectively. The C_p of

materials were recorded by DSC using sapphire as the standard. And C_p of composites were calculated according to the equation: C_p composites = C_p SM ω SM + C_p BNNS ω BNNS, where ω is mass fraction. The ρ of samples were tested using an automatic density analyzer (UltraPYC 1200e, Quantachrome Instruments) at 25 ◦C under helium atmosphere.

2 Materials

PTMEG (Mn = 1000 g/mol, f = 2) was purchased from Aladdin. Isophorone isocyanate (IPDI) was purchased from Adamas. 4, 4′ –Diphenylmethane diisocyanate (MDI) was purchased from Bluestar (China) and used without further purification. 2, 4-Pentanedione dioxime (PDO) was purchased from Titan (China). Dimethylglyoxime (DMG) and dibutyltin dilaurate (DBTDL) and was purchased from Aladdin (China). THF was obtained from Titan and should be redistilled to remove trace moisture before being used. Anhydrous methanol was purchased from adamas-beta. Malonic dihydrazide was purchased from Macklin. 3-Hydroxybenzaldehyde and p-Hydroxybenzaldehyde were purchased from Innochem. Boron Nitride Nanosheets (BNNs, 99.8%, D_{50} 100 nm) was purchased from aladdin (China). Ethanolamine (AR, 99%, Aladdin), Sodium hydroxide (AR, 96%, Aladdin), Hexamethylene Diisocyanate (HDI, 99%, Macklin), N,N-Dimethylformamide (DMF, Dry, 99.8%, Adamas), Dichloromethane (CH_2Cl_2, AR, 99.5%, Innochem), Hydrogen peroxide (30 wt.% in H_2O, Innochem), Deionized water (Deionized water machine, CCH-E20-U).

3. Experimental procedures and characterization data for compounds 3a, 3b, and 3c

3.1 Experimental procedures general procedure for the synthesis of compounds **3a**, **3b**, and **3c**

A seal tube containing malonic acid dihydrazide **1** (5 mmol) and aldehyde 2 (10 mol), then, methanol (50 mL) was added to the system via syringe under an air atmosphere. The reaction mixture was stirred at room temperature until completion of the reaction (monitored by TLC). Then the mixture was distilled under reduced pressure to remove solvent, add ethyl acetate to disperse, wash and filter to obtain the target product **3**.
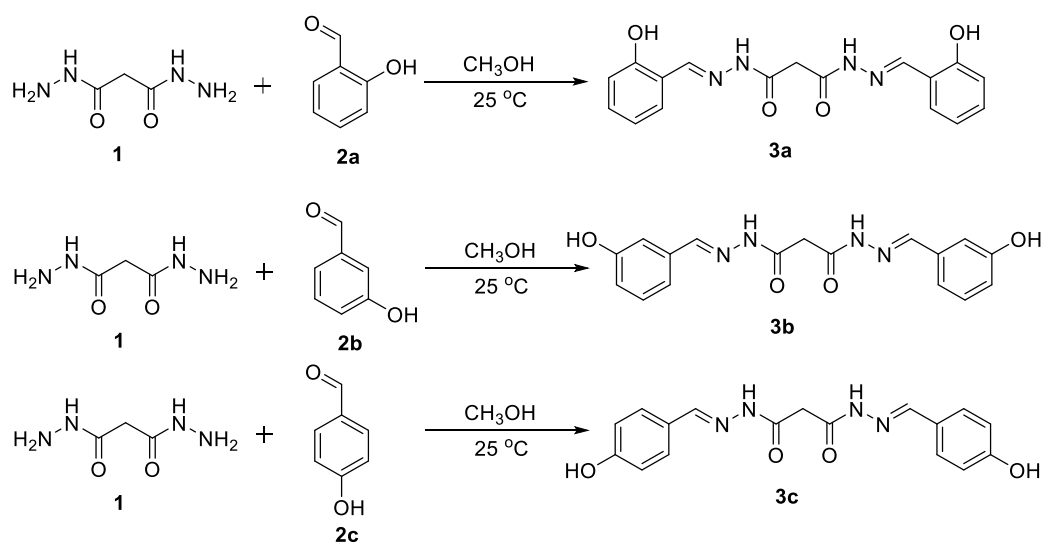
Scheme S1 General procedure for the synthesis of compounds **2a**, **2b**, and **2c**
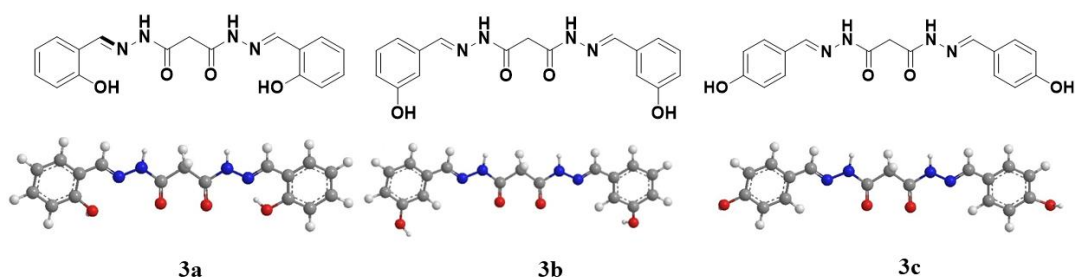
Scheme S2. Structure of ligand **3a – 3c**.

4. Preparation of self-healable polyurethane elastomers

A typical polymerization procedure for the polyurethane elastomers samples is shown in Scheme 2. Here PTMG-2000 (15.00 g, 7.5 mmol) was dispensed in the dried glass vessel equipped with a mechanical stirrer and a mercury thermometer. Subsequently, it was heated to 120 °C under vacuum conditions to remove any residual moisture before being cooled to 80 °C. Next, IPDI (3.5 g, 15 mmol) and DBTDL (0.3 wt%) were added into the vessel and stirred for 3 h under an argon atmosphere to obtain the prepolymer. Then, using a round-bottom flask, ligand (**3a** – **3c**), cerium[III] triflate, and THF were added sequentially to the system via a syringe under a nitrogen atmosphere to obtain a complex solution **(o,m,p)XC** as a chain extender with dynamic bonds (labeled **PU(o,m,p)XC**). Finally, the **(o,m,p)XC** mixture and the BDO acting as the chain extender were added into the vessel and stirred to induce a reaction until the isocyanate (NCO) peak disappeared in the Fourier transform infrared (FTIR) spectra, which required around 40 – 60 min for the **PU(o,m,p)XC** samples. Next, the mixture was poured into a polytetrafluoroethylene mold and reacted further in the oven at 80 °C for 48 h. When the above steps were completed, the samples were left to mature for seven days under ambient conditions before testing. To demonstrate the critical role of the **(o,m,p)XC**, a control sample without phloretin and cerium(III) bonds (labeled **PU(o,m,p)XC**) was prepared using similar steps, with BDO as the diol instead of **PU(o,m,p)XC**. The monomer ratio used during the synthesis of the **PU(o,m,p)XC** samples is shown in Table 1.

5 Preparation of the self-healing thermally conductive polyurethane composite (PUp2CBN)

5.1 Preparation of the Hydroxylated boron nitride (BNNSs-OH)

Hy-BNNSs was prepared as the following method. Disperse of BNNSs (1 g) in the mixed solution of ethanolamine and deionized water (4:1 by volume, 500 ml), ultrasonic dispersion for 4h, centrifuged to remove large particles (10000 r/min) and washed with deionized water several times to remove ethanolamine Then, the obtained product was transferred to a 500 mL flask, 200 mL of 5 mol/L sodium hydroxide and

20 mL of 30% hydrogen peroxide aqueous solution were added in sequence, ultrasonically dispersed for 1 h, and stirred at 80 °C for 12 h. Finally, the reaction mixture was centrifuged, washed, and freeze-dried to obtain the target product BNNSs-OH.

5.2 Preparation of the self-healing thermally conductive polyurethane composite (PUp2CBN)

The self-healing thermally conductive polyurethane composite (**hyBNNs/PUp2C**) was synthesized according to the synthetic method of polyurethane elastomers samples (PUp2C). Here PTMG-2000 (15.00 g, 7.5 mmol) was dispensed in the dried glass vessel equipped with a mechanical stirrer and a mercury thermometer. Subsequently, it was heated to 120 °C under vacuum conditions to remove any residual moisture before being cooled to 80 °C. Next, IPDI (3.5 g, 15 mmol) and DBTDL (0.3 wt%) were added into the vessel and stirred for 3 h under an argon atmosphere, then the HBNNs was added and stirred for another 1 h to obtain the prepolymer. Then, using a round-bottom flask, ligand **3c**, cerium[III] triflate, and THF were added sequentially to the system via a syringe under a nitrogen atmosphere to obtain a complex solution as a chain extender with dynamic bonds (labeled **p2C**). Finally, the **p2C** mixture and the BDO acting as the chain extender were added into the vessel and stirred to induce a reaction until the isocyanate (NCO) peak disappeared in the Fourier transform infrared (FTIR) spectra, which required around 40 – 60 min for the **PUP2C** samples. Next, the mixture was poured into a polytetrafluoroethylene mold and reacted further in the oven at 80 °C for 48 h. When the above steps were completed, the samples were left to mature for seven days under ambient conditions before testing.

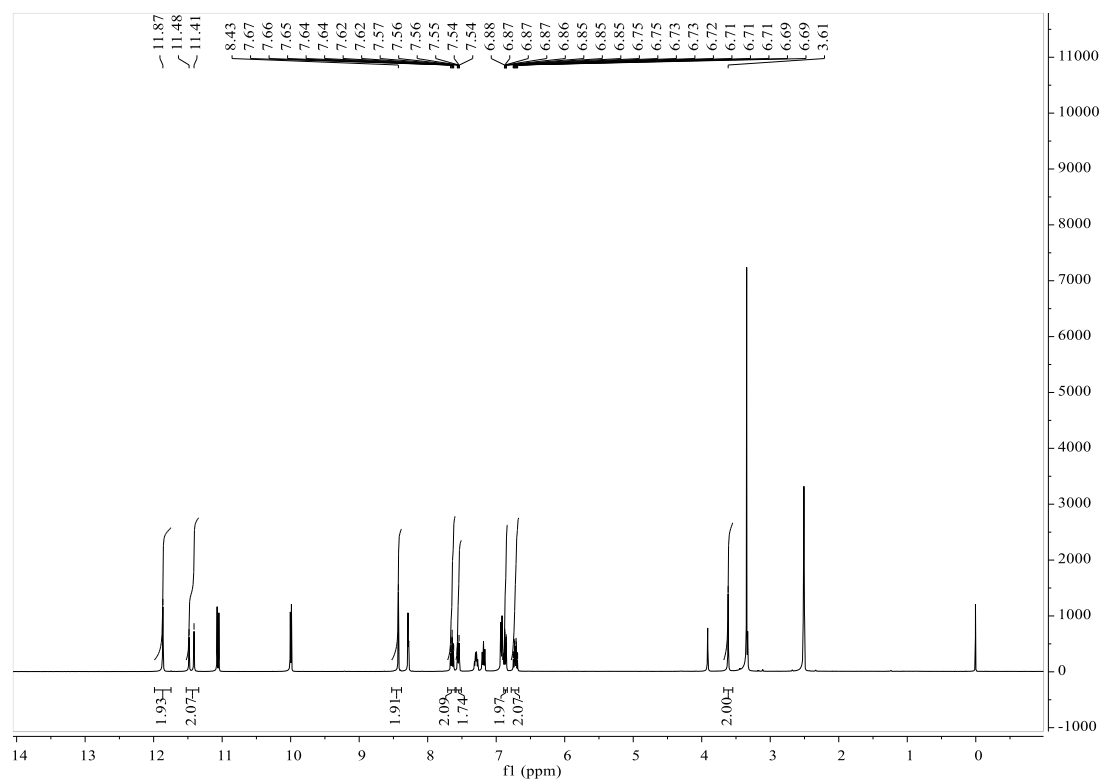**Figure S1.** ^{1}H NMR spectra of compounds **2a**.
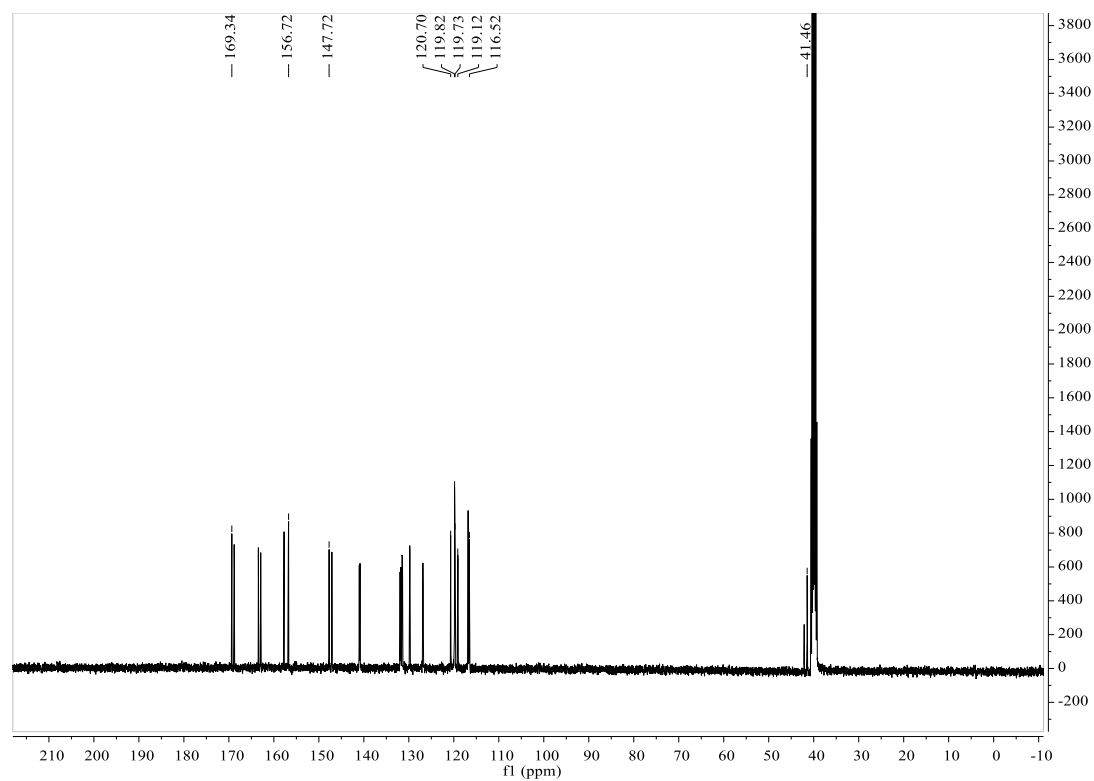

Figure S2. ^{3}C NMR spectra of compounds **2a**.
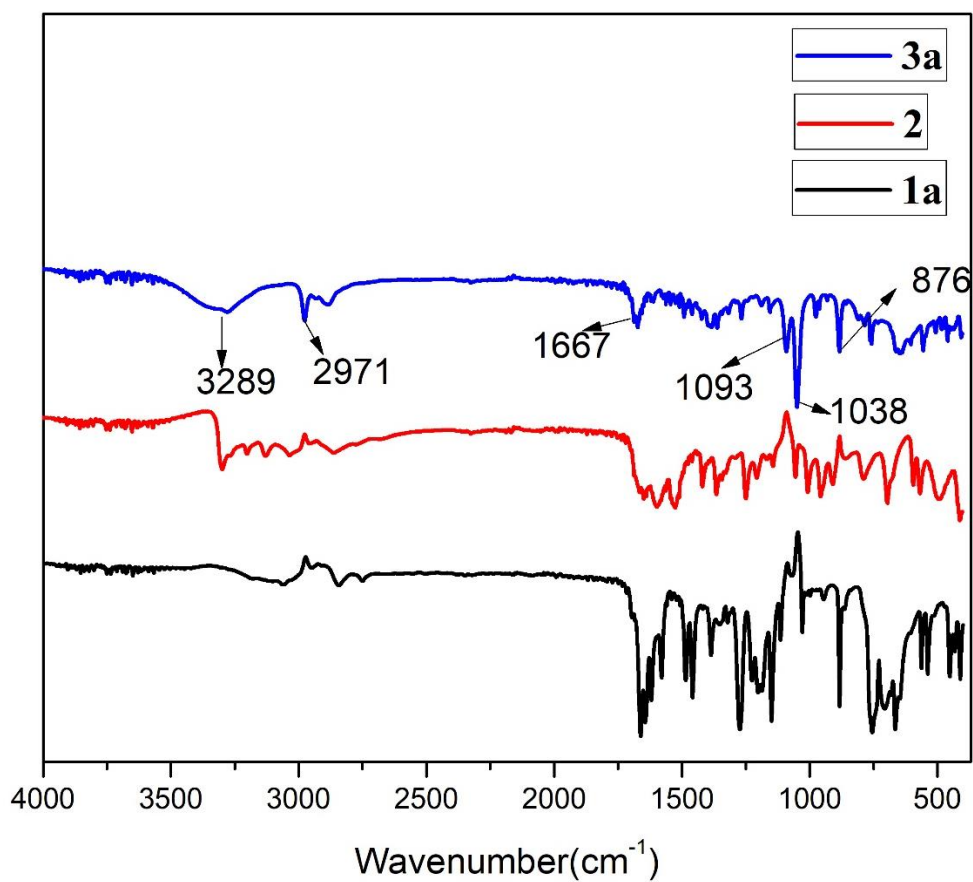
Figure S3. IR spectrum of **2a** in 4000-400 cm^{-1}
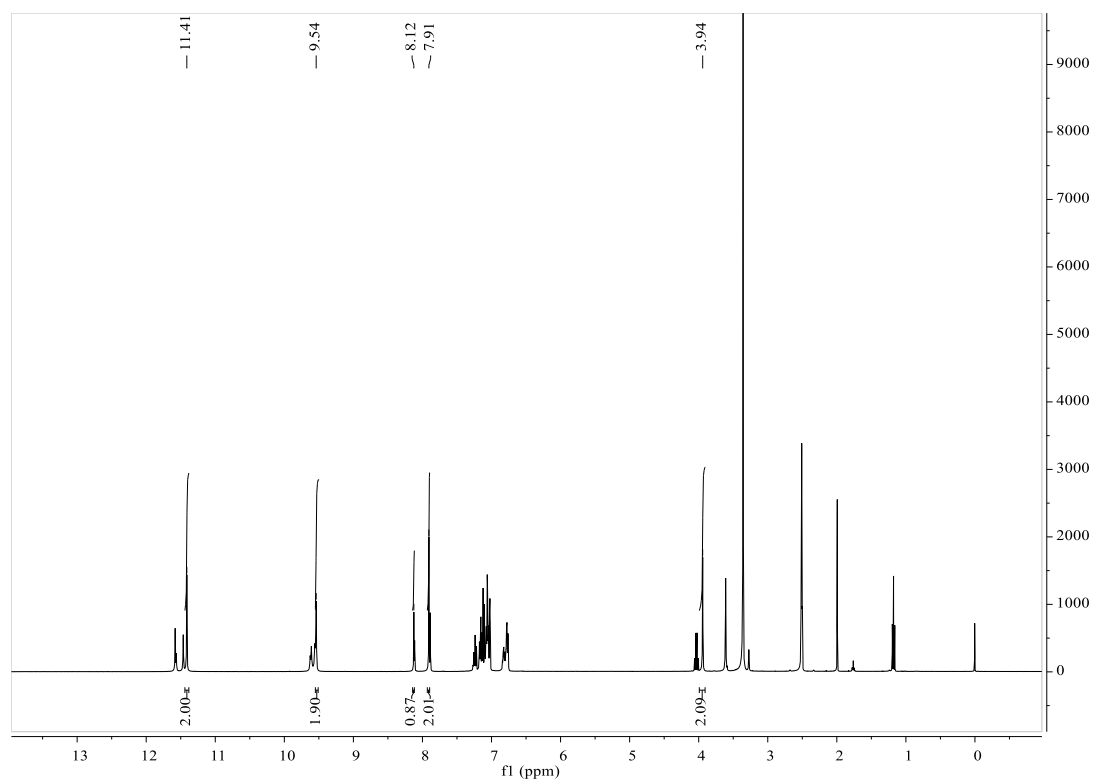

Figure S4. ^{1}H NMR spectra of compounds **2b**.
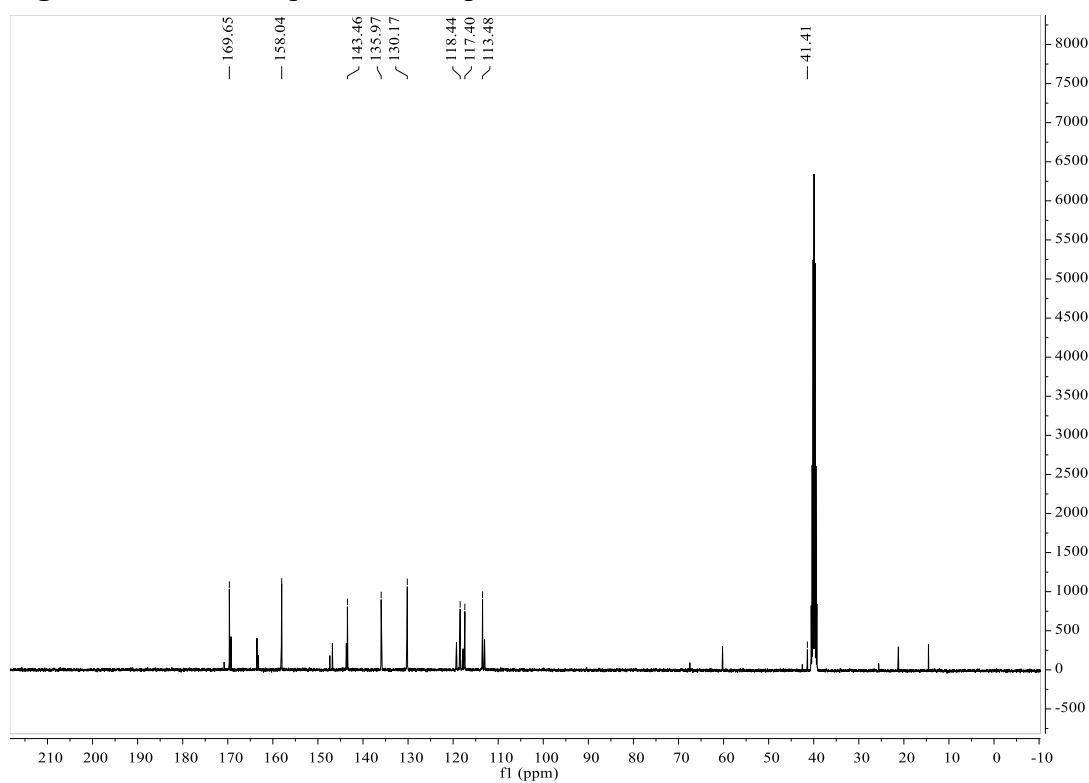
Figure S5. ^{3}C NMR spectra of compounds **2b**.

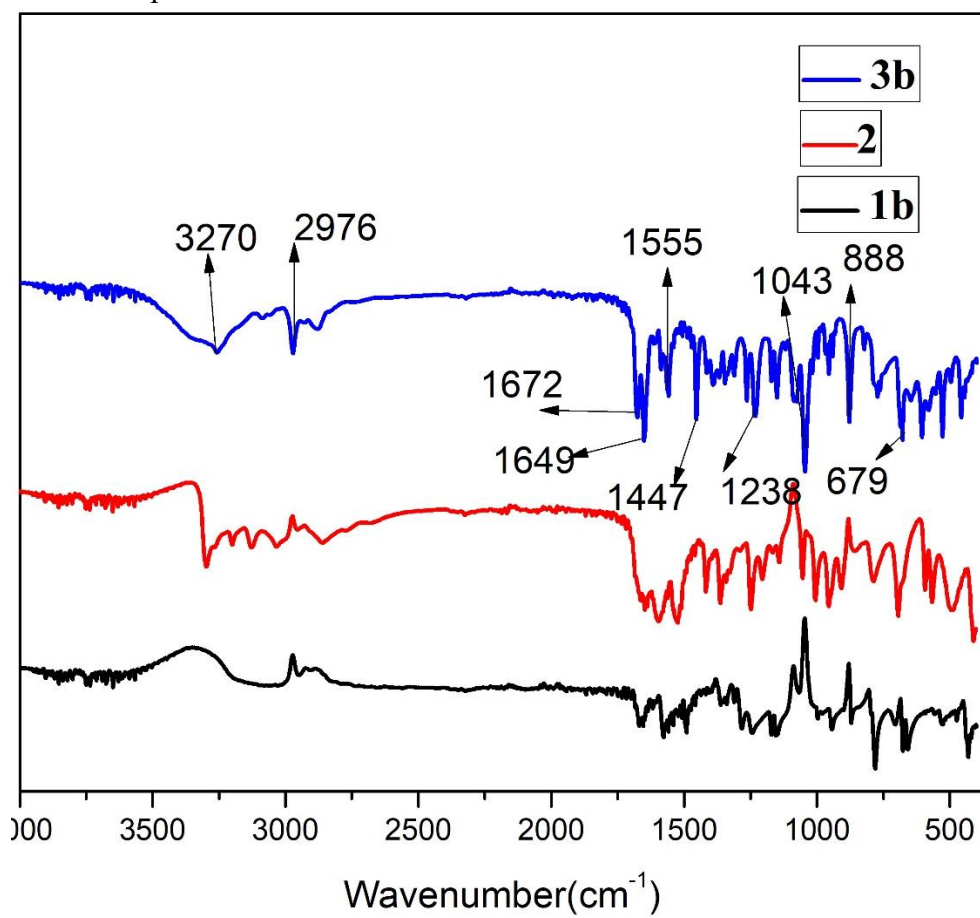
Figure S6. IR spectrum of **2b** in 4000-400 cm^{-1}

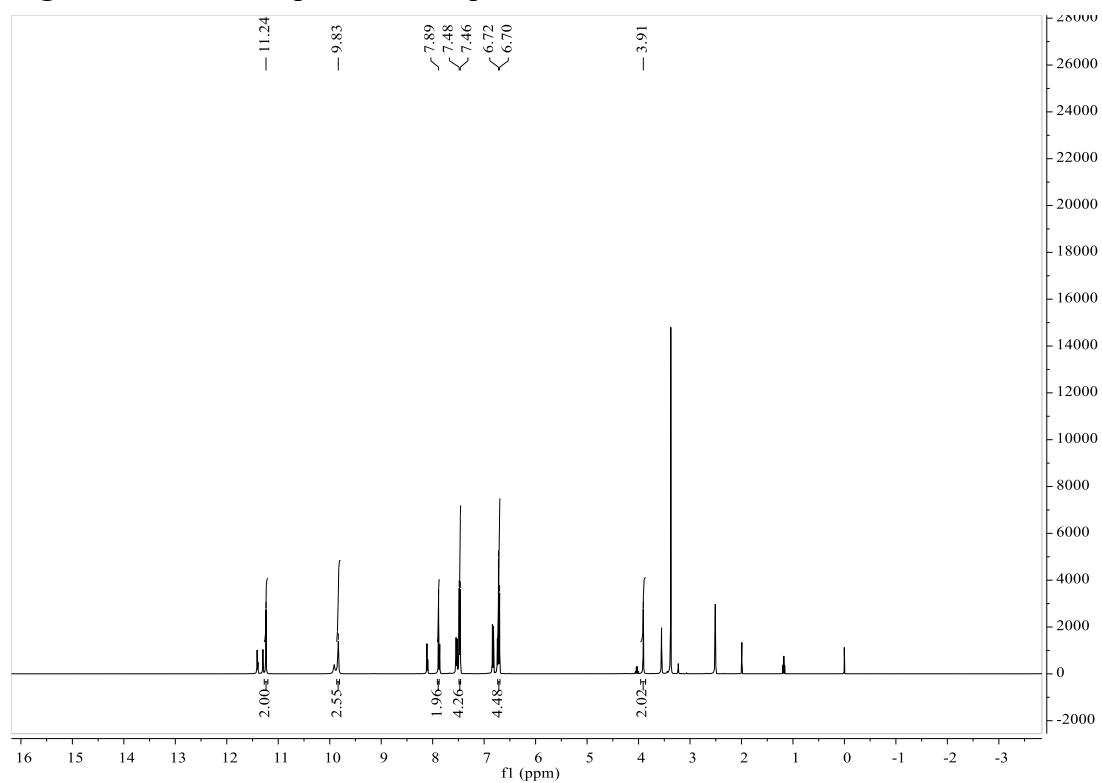**Figure S7.** ^1H NMR spectra of compounds **2c**.

Figure S8. ^3C NMR spectra of compounds **2c**.
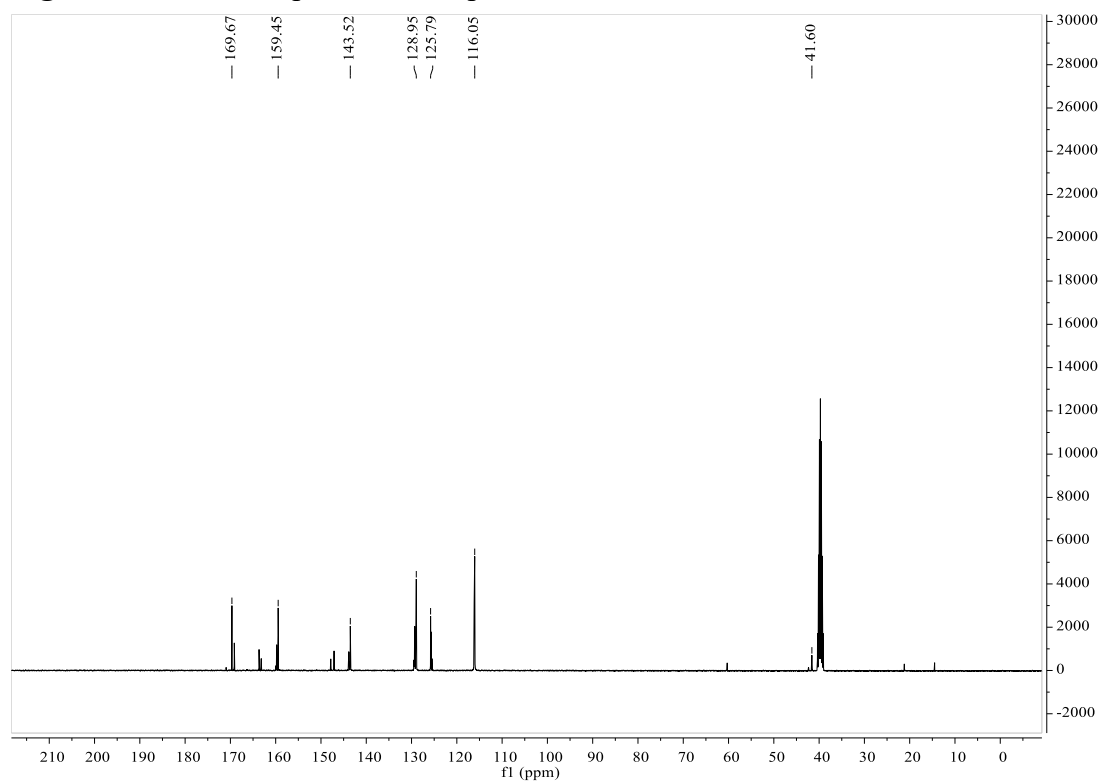
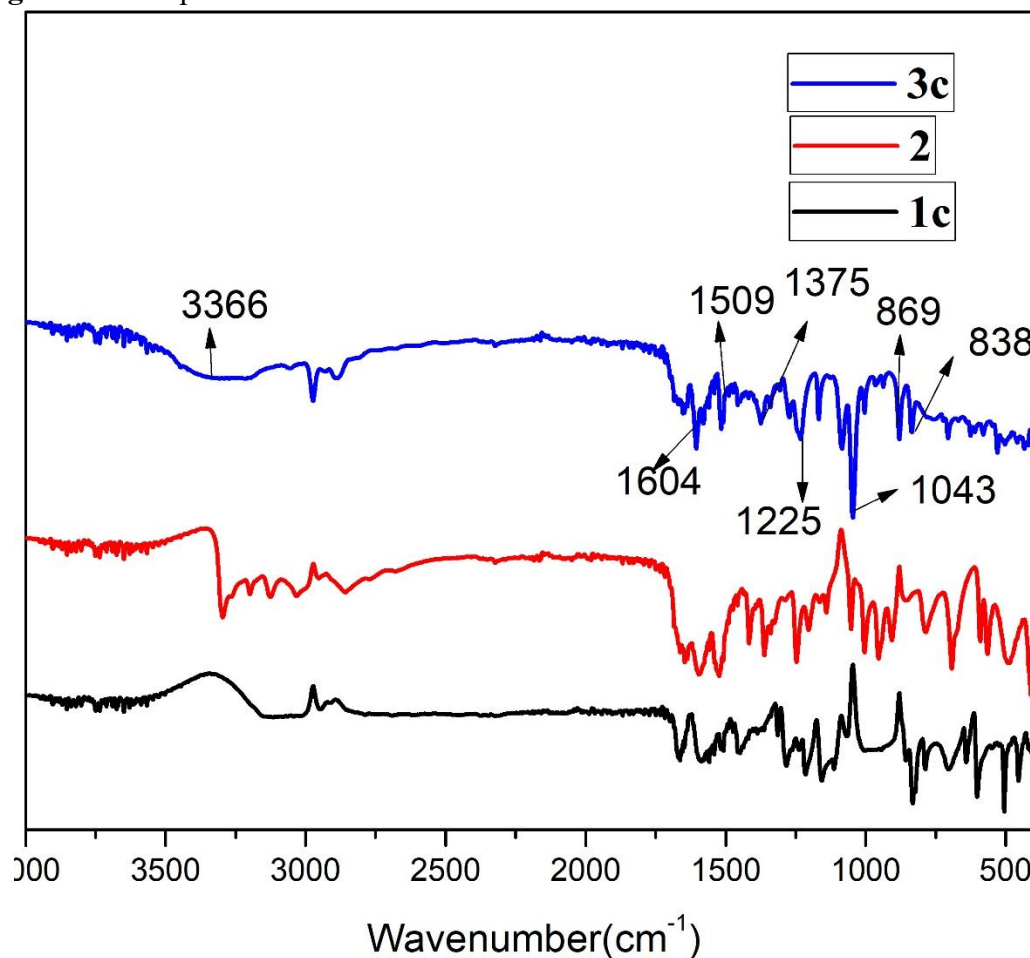**Figure S9.** IR spectrum of **2a** in 4000-400 cm^{-1}

Table S1. Mechanical of our composites and the selected recently reported self-healing thermal conductivity materials.

Publications	Year	Tensile strength (Mpa)	Content of BNNSs (wt%)	thermal conductivity	
				$\lambda_\perp$	$\lambda_{//}$
Wang et al, *Chem. Eng. J.* [1]	2022	6.2	29	0.32	3.8
Zhao et al, *Compos. Sci. Technol.*[2]	2020	0.5	30	0.27	-
Our work	2023	16.4	30	0.41	1.42

[1] D. Wang, S. Ren, J. Chen, Y. Li, Z. Wang, J. Xu, X. Jia, J. Fu, *Chem. Eng. J.* 2022, **430**, 133163.

[2] L. Zhao, X. Shi, Y. Yin, B. Jiang, Y. Huang, Compos. Sci. Technol. 2020, 186, 107919.