# High-strength, high-toughness, self-healing thermosetting shape memory polyurethane enabled by dual dynamic covalent bonds

Xiaoyue Wang[1,2], Jing Xu [1,2], Yaoming Zhang[1], Tingmei Wang[1,2], Qihua Wang[1,2,3], Zenghui Yang[1*] and Xinrui Zhang[1*]

[1]Key Laboratory of Science and Technology on Wear and Protection of Materials, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P.R. China

[2]Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, P.R. China

[3]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

*Corresponding Author(s): Zenghui Yang: yangzh@licp.cas.cn; Xinrui Zhang: xruiz@licp.cas.cn

# Supporting Information

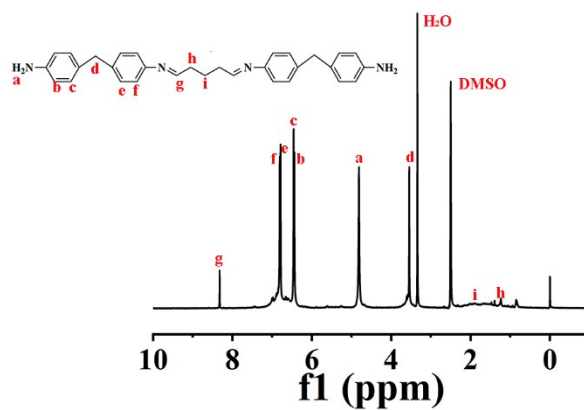## Synthesis of chain extender A and B
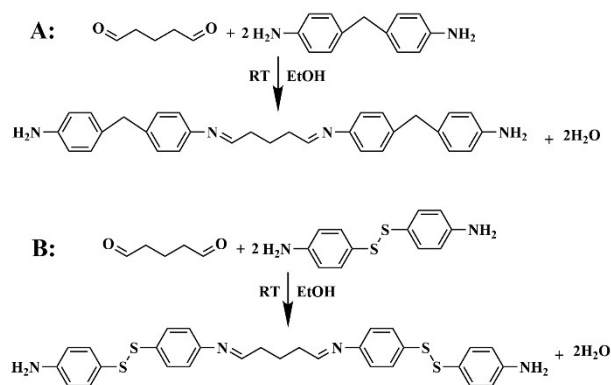


**Scheme S1.** Synthetic route of A and B.



**Figure S1.** $^1$H-NRM spectrum of A: $^1$H NMR (400 MHz, DMSO) δ 8.32 (s, 1H), 6.81(s, 2H), 6.79(s, 2H), 6.46(s, 2H), 6.44(s, 2H), 4.81(s, 2H), 3.54(s, 2H), 1.90(s, 2H), 1.23(s, 2H).
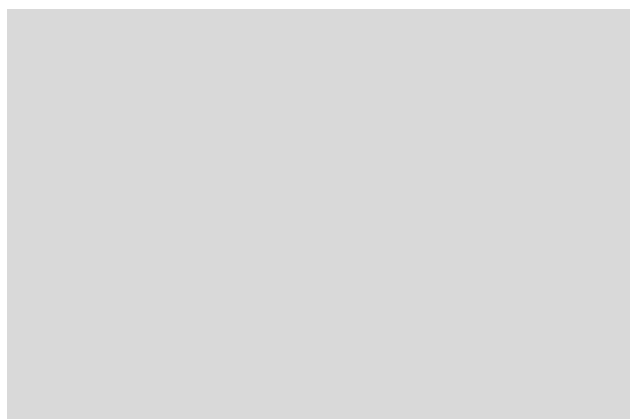
**Figure S2.** ^{1}H-NRM spectrum of B: ^{1}H NMR (400 MHz, DMSO) δ 7.95 (s, 1H), 7.29 (s, 2H), 7.18 (s, 2H), 7.07 (s, 2H), 6.52 (s, 2H), 5.49 (s, 2H), 2.89 (s, 2H), 2.73 (s, 2H).
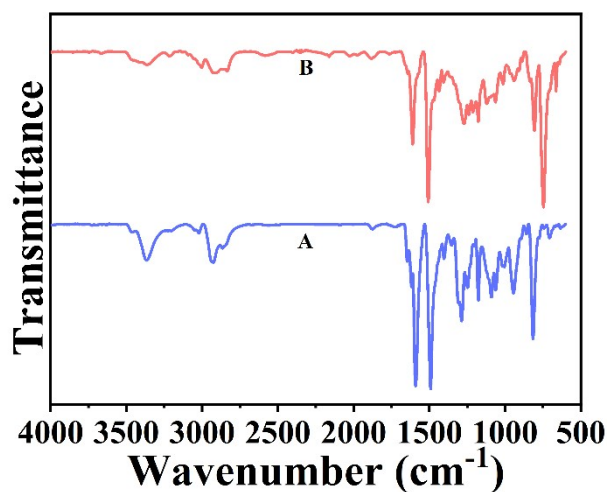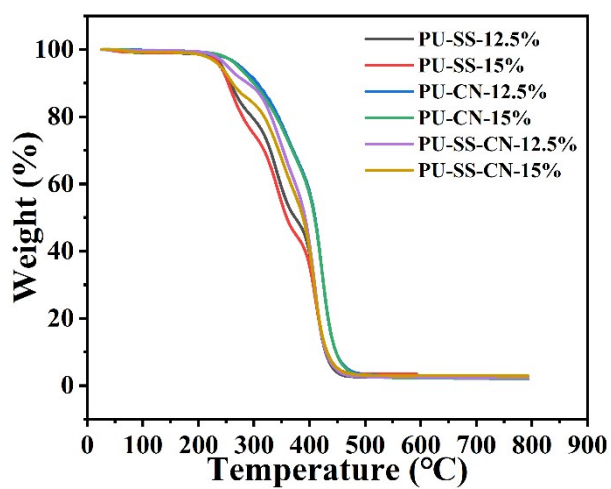


**Figure S3.** FT-IR spectra of A and B.



**Figure S4** TGA curves of PU-SS-12.5%, PU-SS-15%, PU-CN-12.5%, PU-CN-15%,
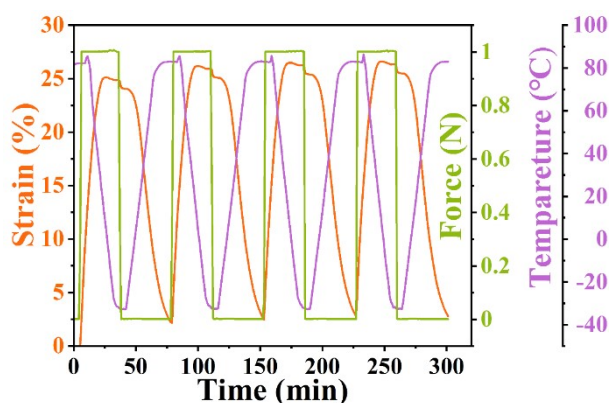
PU-SS-CN-12.5%, and PU-SS-CN-15%.



**Figure S5.** Shape memory cycle curves of PU-SS-12.5%. The PU-SS-12.5% deformed at 60 °C under a loading of 1 N and removed the force after fixing the temporary shape at -60 °C and then recovered the original shape when reheated at 60 °C.



**Figure S6.** Shape memory cycle curves of PU-SS-15%. The PU-SS-15% deformed at 60 °C under a loading of 1 N and removed the force after fixing the temporary shape at -60 °C and then recovered the original shape when reheated at 60 °C.
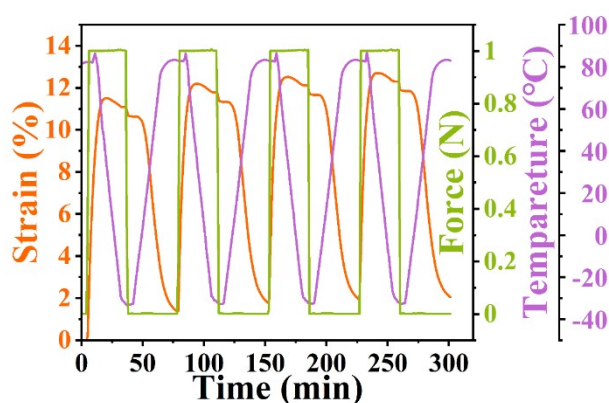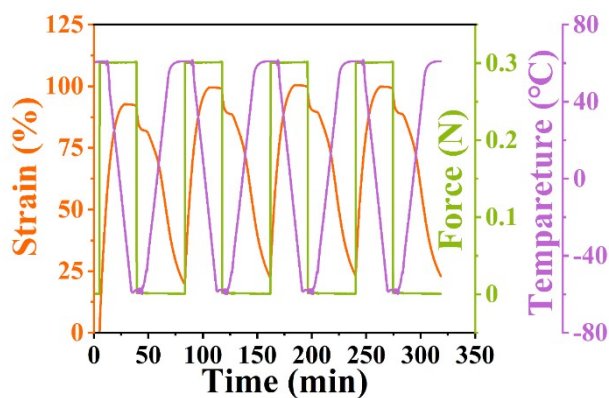


**Figure S7.** Shape memory cycle curves of PU-CN-12.5%. The PU-CN-12.5%

deformed at 60 °C under a loading of 0.3 N and removed the force after fixing the temporary shape at -60 °C and then recovered the original shape when reheated at 60 °C.



**Figure S8.** Shape memory cycle curves of PU-CN-15%. The PU-CN-15% deformed at 60 °C under a loading of 0.3 N and removed the force after fixing the temporary shape at -60 °C and then recovered the original shape when reheated at 60 °C.
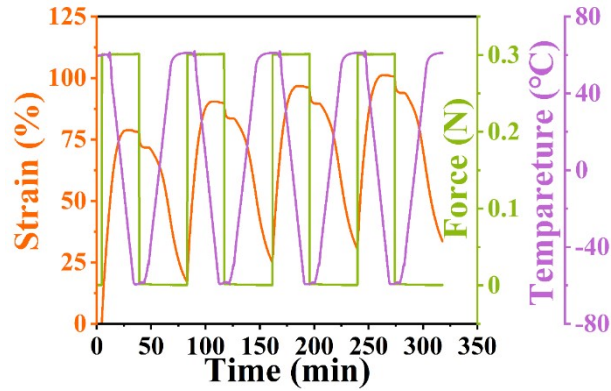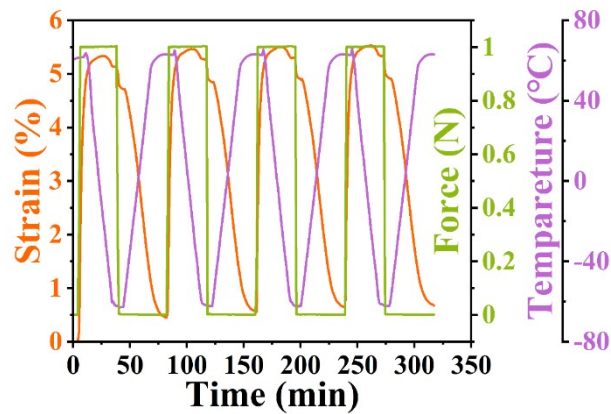


**Figure S9.** Shape memory cycle curves of PU-SS-CN-15%. The PU-SS-CN-15% deformed at 60 °C under a loading of 1 N and removed the force after fixing the temporary shape at -60 °C and then recovered the original shape when reheated at 60 °C.
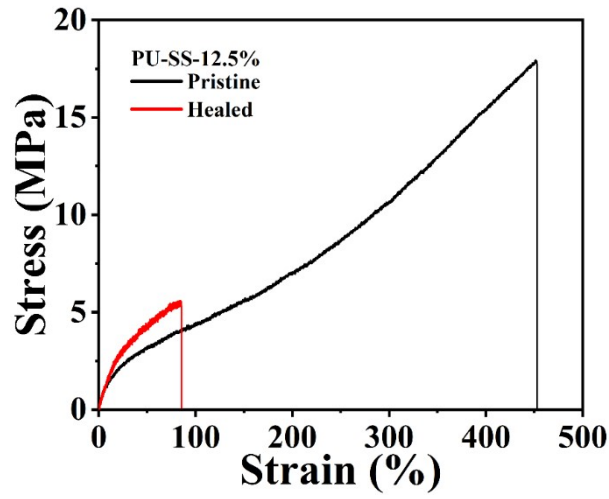
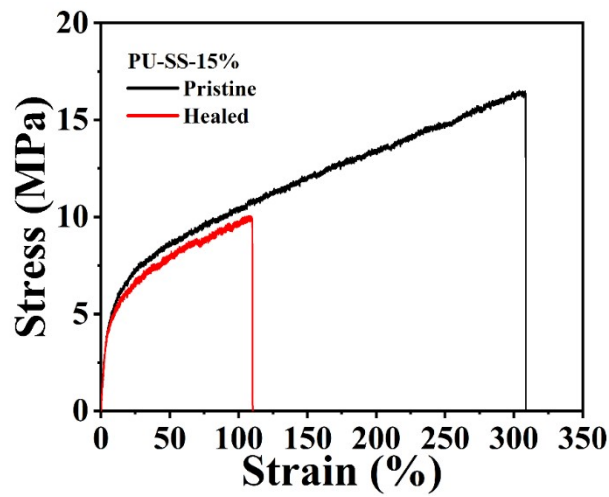**Figure S10** Tensile curves of self-healing test for the PU-SS-12.5%.



**Figure S11** Tensile curves of self-healing test for the PU-SS-15%.
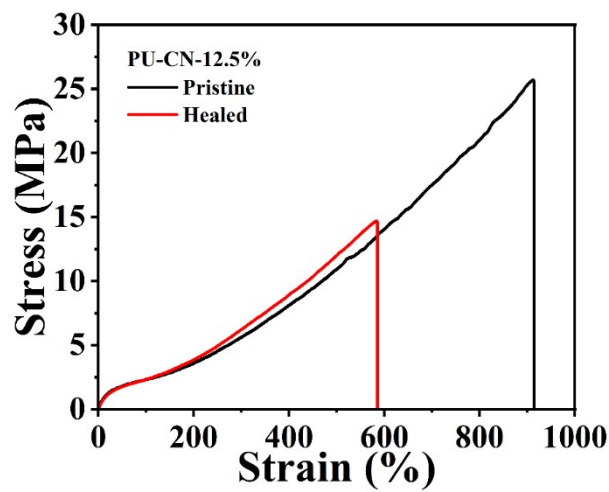


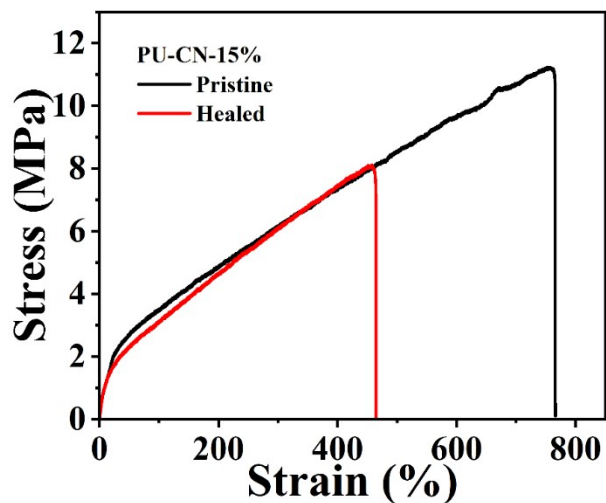**Figure S12** Tensile curves of self-healing test for the PU-CN-12.5%.

**Figure S13** Tensile curves of self-healing test for the PU-CN-15%.
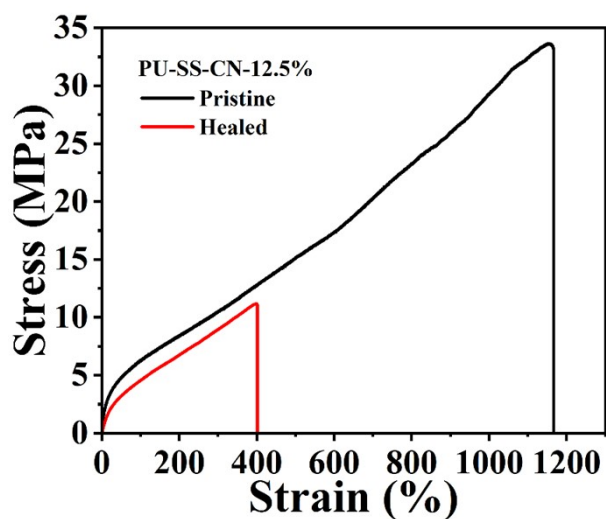


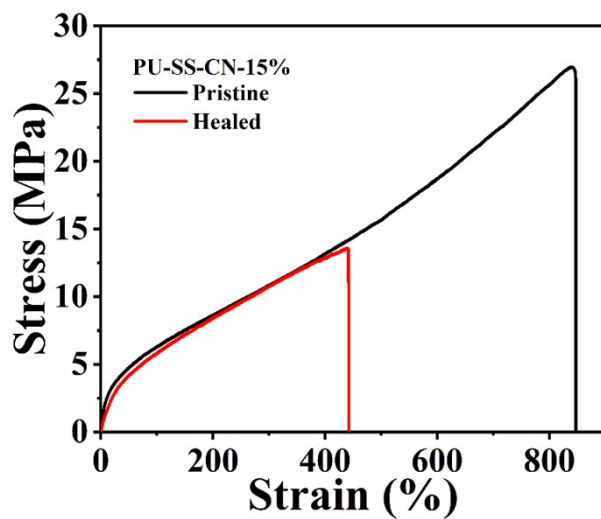**Figure S14** Tensile curves of self-healing test for the PU-SS-CN-12.5%.



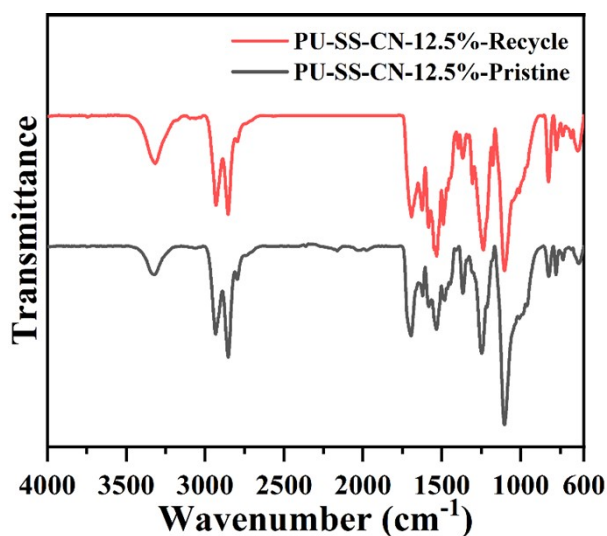**Figure S15** Tensile curves of self-healing test for the PU-SS-CN-15%.

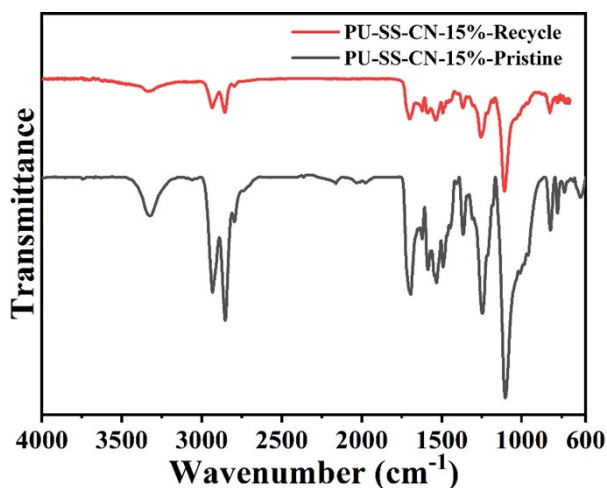**Figure S16** FT-IR of PU-SS-CN-12.5% after hot-pressing.



**Figure S17** FT-IR of PU-SS-CN-15% after hot-pressing.

**Table S1** Summary of the mechanical properties of PU-SS-12.5%, PU-SS-15%, PU-CN-12.5%, PU-CN-15%, PU-SS-CN-12.5%, PU-SS-CN-15%, measured by the tensile tests at the stretching speed of 10 mm/min.

|  | Stress (MPa) | Strain (%) | Young's Modulus (MPa) | Toughness (MJ/m³) |
|---|---|---|---|---|
| **PU-SS-12.5%** | 18.40±1.07 | 465.70±37.13 | 19.24±2.38 | 31.83±8.65 |
| **PU-SS-15%** | 16.86±0.65 | 309.91±10.68 | 132.69±11.52 | 35.93±2.35 |
| **PU-CN-12.5%** | 25.16±0.77 | 940.69±40.98 | 13.40±1.43 | 99.57±0.05 |
| **PU-CN-15%** | 10.09±1.62 | 747.49±25.88 | 19.25±2.20 | 31.66±3.93 |
| **PU-SS-CN-12.5%** | 33.70±4.25 | 1137.72±81.29 | 41.50±4.68 | 197.35±35.33 |
| **PU-SS-CN-15%** | 28.16±1.95 | 822.49±51.07 | 39.90±0.33 | 132.66±15.31 |

**Table S2** $R_f$, and $R_r$ of PU-SS-12.5%, PU-SS-15%, PU-CN-12.5%, PU-CN-15%, PU-SS-CN-15%.

|  | PU-SS-12.5% | PU-SS-15% | PU-CN-12.5% | PU-CN-15% | PU-SS-CN-15% |
|---|---|---|---|---|---|
| $R_f$ | 96.6% | 96.0% | 89.2% | 92.9% | 94.1% |
| $R_r$ | 98.7% | 96.4% | 95.7% | 87.6% | 97.8% |