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Supporting information

Damage-resistant and healable polyacrylonitrile-derived stretchable

materials with exceptional fracture toughness and fatigue threshold

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Figure S1. The thermogravimetric analysis (TGA) of water weight percent trapped within APAN.



Figure S2. FTIR spectra of PAN, APAN and Al³⁺-APAN.¹⁻³ After mixing with Al³⁺, the absorption peak at 926 cm⁻¹ corresponding to N-O group in APAN shifted to a higher wavenumber (943 cm⁻¹) and the absorption intensity of -NH₂ was enhanced, indicating the Al-N coordination interaction was formed.⁴ Besides, the double-peaks for -OH at 3051 and 3164 cm⁻¹, could be observed, which indicated the presence of both coordinated and uncoordinated -OH groups.⁴ Moreover, a new peak for Al-O at

873 cm⁻¹ appeared, further suggesting the successful coordination between Al³⁺ and - OH.^{5, 6} Therefore, the obtained results demonstrated that the coordination between Al³⁺ and amidoxime group was successfully achieved.



Figure S3. Solid-state ²⁷Al-nuclear magnetic resonance (NMR) spectrum of Al³⁺-APAN.^{4, 7, 8}



Figure S4. UV-vis spectra of APAN and Al³⁺-APAN.



Figure S5. SEM image and its corresponding EDS element maps of the dried Al^{3+} -APAN (the scale bar is 7 μ m).



Figure S6. The modulus and work of extension results of PAN, 84 mg Al³⁺-APAN (1), 126 mg Al³⁺-APAN (2), and 168 mg Al³⁺-APAN (3).



Figure S7. TGA curve of Al³⁺-APAN. Since the final evaporation temperature of DMF is around 250 °C,⁹ the obtained DMF contents for Al³⁺-APAN, therefore, was about 25.8%.



Figure S8. (a) and (b) SEM images of Al³⁺-APAN, (c) the size distribution of the holes on Al³⁺-APAN.



Figure S9. Tensile curves of Al³⁺-APAN with different molecular weight.



Figure S10. Repeated fracture toughness tests of Al³⁺-APAN.



Figure S11. Optical microscopic images of notched Al^{3+} -APAN before and after stretching. The scar bar is 200 µm.



Figure S12. (a) Maximum stress and energy release rate *G* during the cyclic testing of the unnotched samples when loading to 25%, 50%, 100%, 150% and 200% strain for 3500 cycles, (b) DMF content of Al^{3+} -APAN sample after being stretched for 3500 cycles at a strain of 200%, indicating that the content of DMF was generally well-maintained during fatigue test. During cyclic test, the maximum stress of samples after the 2500th cycle generally reached the steady state already. Herein, the stretching curves of the 3000th cycle were used to calculate the *G* values.



Figure S13. Repeated tests for the determination of fatigue threshold.



Figure S14. XRD results of pure PAN and Al³⁺-APAN.



Figure S15. (a) and (b) the optical microscopic images for Al³⁺-APAN before and after healing for 30 min at 60 °C, and (c) SEM image for the wound of healed Al³⁺-APAN.



Figure S16. (a) Loading-unloading tests of healed Al³⁺-APAN at different strains, (b) energy dissipation results at different strains obtained from (a), (c) load-displacement curves from fracture tests of healed Al³⁺-APAN, and (d) the tensile curves for original

and healed Al³⁺-APAN.



Figure S17. The schematic diagram of impedance spectroscopy test for Al³⁺-APAN and the conductivity was calculated to be 0.0356 S m⁻¹. The conductivity (δ) was calculated by the following formula: $\delta = L / ((R-R') \times S)$, where R is the resistance of two stainless steels (3.3 Ω) and Al³⁺-APAN, R' is the resistance of stainless steel, L is the thickness of Al³⁺-APAN (0.38 mm) and S is the surface area of Al³⁺-APAN (7.1 mm x 8.0 mm).

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