**Supporting Online Materials**

Facile UV-Repairable Polyethylenimine-Copper (C$_2$H$_5$N-Cu) Supramolecular Polymer Networks

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Materials and Methods

Materials: Polyethylenimine (PEI, Mn=10000, Mw=25000, repeated unit: C$_2$H$_5$N) and Copper sulfate pentahydrate were purchased from Sigma Aldrich Co.

Preparation of Polyethylenimine-Copper Sulfate (C$_2$H$_5$N-Cu) Supramolecular Polymer Networks: PEI and CuSO$_4$ water solution were prepared by dissolving PEI and CuSO$_4$ in water directly. The PEI and CuSO$_4$ solutions are colorless and blue respectively (Figure S1A-a, -b; Figure S1B-a, -b). The C$_2$H$_5$N-Cu solution was prepared by mixing PEI and CuSO$_4$ water solutions, while stirring at room temperature for 24 h. Upon mixing, solution color changes to dark blue, which confirms the formation of C$_2$H$_5$N-Cu complexes$^{[1]}$ (Figure S1A-c, Figure S1B-c). C$_2$H$_5$N-Cu supramolecular network films were prepared by casting aqueous C$_2$H$_5$N-Cu solution onto the glass, gold and PTFE substrates followed by drying at room temperature for 24 hrs. The final step involved drying at 50 °C for 48 hrs. Figure S2 shows a comparison of ATR-FTIR spectra of C$_2$H$_5$N-Cu supramolecular polymer network with PEI and CuSO$_4$. The band at 1658 cm$^{-1}$ is due to associated N-H stretching vibrations, which confirms the formation of the Cu-
N coordination bond.\[2\] The overlapping bands at 1093 cm\(^{-1}\) also confirm this behavior (Figure S2). Further evidence for C\(_2\)H\(_5\)N-Cu supramolecular network formation is shown in Raman spectra (Figure S3). CuSO\(_4\) exhibits three vibration modes (Figure S3, trace a): asymmetric stretching vibrations at 1208, 1097, 1043, and 1019 cm\(^{-1}\); the out-of-plane bending vibrations at 666, 626, and 607 cm\(^{-1}\); the in-plane bending vibrations at 502 and 425 cm\(^{-1}\).\[3\] Symmetric stretching band at 972 cm\(^{-1}\) due to free sulfate is detected in the spectra of C\(_2\)H\(_5\)N-Cu supramolecular network\[4\] (Figure S3, trace c), demonstrating that all the Cu\(^{2+}\) ions are coordinated with N of PEI. In addition, the new band at 458 cm\(^{-1}\) is attributed to Cu-N coordination bonds\[2\].

Exposure to UV radiation was conducted using a 120 W fluorescent UV lamp of 302 nm wavelength of light. Each specimen was placed 5 cm from the UV source.

UV-Vis absorption spectra were measured using a Varian Cary 500 scan UV-Vis-NIR Spectrophotometer in the wavelength range from 190 nm to 1100 nm. In a typical test for solution, PEI, CuSO\(_4\) and C\(_2\)H\(_5\)N-Cu solution were placed in a quartz cell with a 10 mm pathlength; for film, C\(_2\)H\(_5\)N-Cu solution were evaporated to form solid films that were attached on a quartz substrate with 0.5 mm pathlength.

Thermal analysis of the C\(_2\)H\(_5\)N-Cu network was conducted using TA Instruments DSC Q-100. The calibration was carried out using indium and sapphire standards. Heating and cooling rates of 10 °C/min were used over the studied temperature range of -80 °C-60 °C.

Microscopic attenuated total reflectance Fourier transform infrared (\(\mu\)ATR FT-IR) spectra were obtained using a Bio-Rad FTS-6000 FTIR single-beam spectrometer at 4 cm\(^{-1}\) resolution. A 2 mm Ge crystal, with a 45° face angle maintaining constant contact pressure between crystal and specimens was used. All spectra were corrected for spectral distortions and optical effects using
Urban-Huang algorithm\cite{5}. Internal reflection infrared (IRIR) images were obtained using a Bio-Rad FTS 7000 Stingray system equipped with internal reflection IR imaging (IRIRI) providing 1 micron spatial resolution. This system consists of a Bio-Rad FTS 7000 spectrometer, a Varian 600 UMA microscope, an image IR focal plane array (FPA) image detector, and internal reflection IR imaging. IR images were collected using the following spectral acquisition parameters: under sampling ratio 2, rapid-scan speed 5Hz, number of images per step 64, and spectral resolution 4 cm\(^{-1}\). In a typical experiment, spectral data set acquisition time was 1 min and image processing was performed using ENVI software (The Environment for Visualizing Images, Research Systems, Inc.) v. 3.5.

Raman spectra were obtained using a Renishaw Raman microscope equipped with a computer controlled three-axis encoded (X, Y, Z) motorized stage, a RenCam CCD detector, and a Leica microscope (DMLM series). The 785 nm diode laser provided an excitation source with a maximum power output of 300 mW. The films were placed on the gold surface and each Raman spectrum was collected at a 100 mW laser power and an acquisition time of 10 sec.
Figure S1 illustrates optical images of mechanically damaged C$_2$H$_5$N-Cu supramolecular polymer networks with the C$_2$H$_5$N:Cu molar ratio of 60 (Specimen B of Figure 3 in the main document. As seen, longer exposure times results in complete self-healing.

![Optical images](image)

**Figure S1.** Optical images of mechanically damaged C$_2$H$_5$N-Cu supramolecular polymer networks with the C$_2$H$_5$N:Cu molar ratio of 60 (Specimen B of Figure 3 in the main document.

![Absorption spectra and optical images](image)

**Figure S2** UV-Vis absorption spectra (A) and optical images (B) of PEI (a), CuSO$_4$ (b), and C$_2$H$_5$N-Cu complex networks (c).

Figure S2, A illustrate absorption spectra of PEI (a), CuSO$_4$ (b) and C$_2$H$_5$N-Cu (c) in water. Pure PEI has no absorption bands in UV-Vis region (trace a); it is a colorless substance (Figure S2-B). CuSO$_4$ water solution has two absorption band at 277 and 789 nm (Figure S2, A-b); blue-green
solution (Figure S2-B). Trace c of Figure S2, A illustrates UV-Vis spectra of C$_2$H$_5$N-Cu solution, with two absorption bands at 274 nm and 626 nm; deep blue color (Figure S2-B). The shift of the absorption band is induced by bonding $\sigma$(N)→antibonding d$_{x^2-y^2}$(Cu) charge transfer.$^{[6]}$ These observations confirms formation of C$_2$H$_5$N-Cu complexes.

![Figure S3 ATR-FTIR spectra of CuSO$_4$ (a), PEI (b) and C$_2$H$_5$N-Cu supramolecular polymer networks (c).](image)

**Figure S3** ATR-FTIR spectra of CuSO$_4$ (a), PEI (b) and C$_2$H$_5$N-Cu supramolecular polymer networks (c).

Figure S3 illustrates ATR-FTIR spectra of CuSO$_4$ (a), PEI (b) and C$_2$H$_5$N-Cu supramolecular polymer networks (c). The bands at 1093, 1049 and 1119 cm$^{-1}$ in Trace a and b due to the stretching vibration of S-O and C-N bonds exhibit overlap in trace c. The 1658 cm$^{-1}$ band due to associated N-H vibrations increases significantly upon C$_2$H$_5$N-Cu complex formation. These observations confirm the formation of C$_2$H$_5$N-Cu complex networks.
**Figure S4** Raman spectra of CuSO₄ (a), PEI (b) and C₂H₅N-Cu supramolecular polymer networks (c).

Figure S4 shows Raman spectra of CuSO₄ (a), PEI (b) and C₂H₅N-Cu supramolecular polymer networks (c). CuSO₄ (trace a) exhibits asymmetric stretching vibrations at 1208, 1097, 1043, and 1019 cm⁻¹, out-of-plane bending vibrations at 666, 626, and 607 cm⁻¹, and in-plane bending vibrations at 502 and 425 cm⁻¹.[3] When C₂H₅N-Cu complexes are formed, only symmetric stretching vibrations at 972 cm⁻¹ corresponding to S-O are observed[4], indicating that all of Cu²⁺ are coordinated with amine groups of PEI. The new band at 458 cm⁻¹ is attributed to Cu-N coordination bonds[2], further confirming formation of coordinated supramolecular polymer network.
**Figure S5** Modulated differential scanning calorimetry (MDSC) of PEI (a) and C$_2$H$_5$N-Cu supramolecular polymer networks (b).

Figure S5 illustrates modulated differential scanning calorimetry (MDSC) thermograms of PEI (a) and C$_2$H$_5$N-Cu supramolecular polymer networks (b). When CuSO$_4$ is added to PEI, T$_g$ of PEI increases from -53 to -35 °C, thus indicating formation of the C$_2$H$_5$N-Cu supramolecular polymer network.
Figure S6 Square-planar and tetrahedral configurations for \( \text{C}_2\text{H}_5\text{N-Cu} \) complexes formed in \( \text{C}_2\text{H}_5\text{N-Cu} \) supramolecular polymer networks.

Figure S6 shows two configurations of \( \text{C}_2\text{H}_5\text{N-Cu} \) complex. Upon UV exposure, the \( \text{C}_2\text{H}_5\text{N-Cu} \) coordination geometry undergoes square-planar to tetrahedral configuration changes with large atomic movements and backbone alkyl group distortion, which results in volume changes\[^7\].
Figure S7 X-ray diffraction patterns of CuSO₄ (A), glass substrate (B) and damaged C₂H₅N-Cu supramolecular polymer networks (C) as a function of UV exposure. a) 0 h; b) 1 h; c) 3 h.

Figure S7, A and B, illustrate X-ray diffraction patterns of CuSO₄ and glass substrate, respectively. CuSO₄ exhibits a diffraction peak at 2Θ = 32.8°, while glass substrate has a broad diffraction at 2Θ = 24.6°. X-ray diffraction patterns of damaged C₂H₅N-Cu supramolecular networks as a function of UV exposure are shown in Figure S7, C. Because of Cu-N
coordination, no diffraction peaks due to pure CuSO$_4$ are detected, thus supporting Raman data shown in Figure S4. Reflections at $2\Theta = 11.2^\circ$ confirm the formation of C$_2$H$_5$N-Cu supramolecular networks.$^{[5]}$ With the increased UV exposure, $2\Theta$ at $11.2^\circ$ shifts to $10.1^\circ$, indicating configuration changes from a square-planar to distorted tetrahedral geometry$^{[8]}$. This configuration change results in unit cell expansion and volume increase, reflected by a gradual $11.2^\circ$ peak shift towards lower angles$^{[9]}$ (Figure S7, C).
**Figure S8** ATR-FTIR spectra of undamaged C$_2$H$_5$N-Cu supramolecular polymer networks as a function of UV exposure time: a) 0 h; b) 1 h; c) 3 h.

Figure S8 illustrates ATR-FTIR spectra of undamaged C$_2$H$_5$N-Cu supramolecular polymer networks as a function of UV exposure. With the increased UV exposure time, undamaged C$_2$H$_5$N-Cu networks show no spectral changes, indicating that only damaged areas are affected by UV exposure.
Figure S9 X-ray diffraction patterns of the \( \text{C}_2\text{H}_5\text{N}-\text{Cu} \) supramolecular polymer networks. a, \( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 80 \); b, \( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 60 \); c, \( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 40 \); d, \( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 30 \); e, \( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 20 \).

Figure S9 shows X-Ray diffraction of \( \text{C}_2\text{H}_5\text{N}-\text{Cu} \) supramolecular polymer networks with the following \( \text{C}_2\text{H}_5\text{N}-\text{Cu} \) molar ratios: 80 (a), 60 (b), 40 (c), 30 (d), 20 (e). Intensity of the diffraction peaks at \( 2\theta = 11.2^\circ \) increases with the decreased \( \text{C}_2\text{H}_5\text{N}-\text{Cu} \) molar ratio, demonstrating that more \( \text{C}_2\text{H}_5\text{N}-\text{Cu} \) complexes are formed at lower \( \text{C}_2\text{H}_5\text{N}-\text{Cu} \) molar ratio. Cross-linking degree of this \( \text{C}_2\text{H}_5\text{N}-\text{Cu} \) supramolecular polymer networks depends on the content of \( \text{C}_2\text{H}_5\text{N}-\text{Cu} \) coordination, therefore the network cross-linking density increases with the decreased \( \text{C}_2\text{H}_5\text{N}-\text{Cu} \) molar ratio.
Figure S10 Optical images of mechanically damaged \( \text{C}_2\text{H}_5\text{N} \)-Cu supramolecular polymer networks. A1, A2, A3 and A4 are optical images heated at 50 °C for 0, 6, 24 and 48 hrs (\( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 80 \)); B1, B2, B3 and B4 are optical images heated at 50 °C for 0, 6, 24 and 48 hrs (\( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 60 \)); C1, C2, C3 and C4 are optical images heated at 50 °C for 0, 6, 24 and 48 hrs (\( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 40 \)); D1, D2, D3 and D4 are optical images heated at 50 °C for 0, 6, 24 and 48 hrs (\( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 30 \)); E1, E2, E3 and E4 are optical images heated at 50 °C for 0, 6, 24 and 48 hrs (\( \text{C}_2\text{H}_5\text{N}:\text{Cu} = 20 \)).

Figure S10 illustrates self-healing behavior of mechanically damaged \( \text{C}_2\text{H}_5\text{N} \)-Cu supramolecular polymer networks with the following \( \text{C}_2\text{H}_5\text{N}:\text{Cu} \) molar ratios at 50 °C: 80 (A1-A4), 60 (B1-B4), 40 (C1-C4), 30 (D1-D4), 20 (E1-E4). At this temperature, all of the \( \text{C}_2\text{H}_5\text{N} \)-Cu supramolecular polymer networks can not be repaired. Since the actual sample temperature is ~ 30 °C after UV exposure, the self-healing is not caused by heat but activation of the Cu-N coordination bonds.
Figure S11 Optical images of mechanically damaged C$_2$H$_5$N-Cu supramolecular polymer networks. A1, A2, A3 and A4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C$_2$H$_5$N:Cu = 80); B1, B2, B3 and B4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C$_2$H$_5$N:Cu = 60); C1, C2, C3 and C4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C$_2$H$_5$N:Cu = 40); D1, D2, D3 and D4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C$_2$H$_5$N:Cu = 30); E1, E2, E3 and E4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C$_2$H$_5$N:Cu = 20).

Figure S11 illustrates self-healing behavior of the mechanically damaged C$_2$H$_5$N-Cu supramolecular polymer networks with the following C$_2$H$_5$N:Cu molar ratios at 75 °C: 80 (A1-A4), 60 (B1-B4), 40 (C1-C4), 30 (D1-D4), 20 (E1-E4). At this temperature, only low cross-linked films (C$_2$H$_5$N-Cu molar ratio ≥ 40) can be repaired, which also identifies that the self-healing upon UV exposure is not caused by heat but activation of the Cu-N coordination bonds.
References


