Supporting Online Materials

Facile UV-Repairable Polyethylenimine-Copper (C_2H_5N-Cu) Supramolecular Polymer Networks

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Materials and Methods

Materials: Polyethylenimine (PEI, Mn=10000, Mw=25000, repeated unit: C_2H_5N) and Copper sulfate pentahydrate were purchased from Sigma Aldrich Co.

Preparation of Polyethylenimine-Copper Sulfate (C_2H_5N-Cu) Supramolecular Polymer Networks: PEI and $CuSO_4$ water solution were prepared by dissoving 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_2H_5N-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_2H_5N-Cu compelxes[1] (Figure S1A-c, Figure S1B-c). C_2H_5N-Cu supramolecular network films were prepared by casting aqueous C_2H_5N-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 comparision of ATR-FTIR spectra of C_2H_5N-Cu supramolecular polymer network with PEI and $CuSO_4$. The band at 1658 cm^{-1} is due to associated N-H streching vibrations, which confims 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_2H_5N-Cu supramolecular network formation is shown in Raman spectra (Figure S3). $CuSO_4$ exhibits three vibration modes (Figure S3, trace a): asymmetric streching 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 streching band at 972 cm^{-1} due to free sulfate is detected in the spectra of C_2H_5N-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_2H_5N-Cu solution were placed in a quartz cell with a 10 mm pathlength; for film, C_2H_5N-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_2H_5N-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 ^{o}C-60 ^{o}C.

Microscopic attenuated total reflectance Fourier transform infrared (μATR 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^{o} 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[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_2H_5N-Cu supramolecular polymer networks with the C_2H_5N:Cu molar ratio of 60 (Specimen B of Figure 3 in the main documant. As seen, longer exposure times results in complete self-healing.

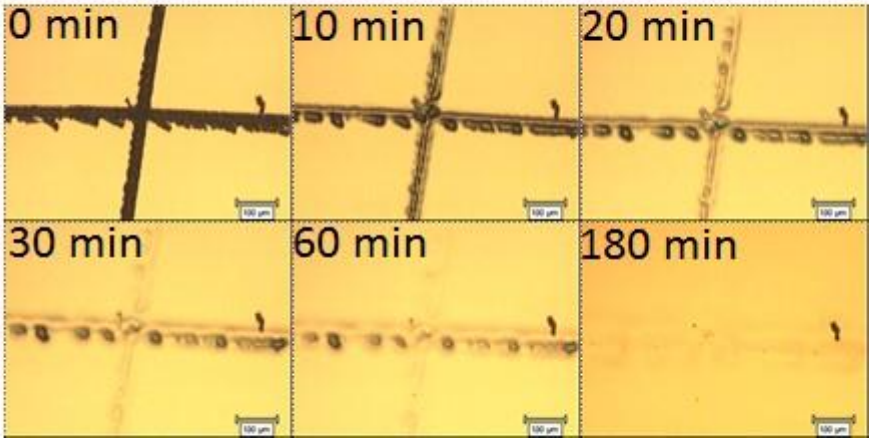

Figure S1. Optical images of mechanically damaged C_2H_5N-Cu supramolecular polymer networks with the C_2H_5N:Cu molar ratio of 60 (Specimen B of Figure 3 in the main documant.

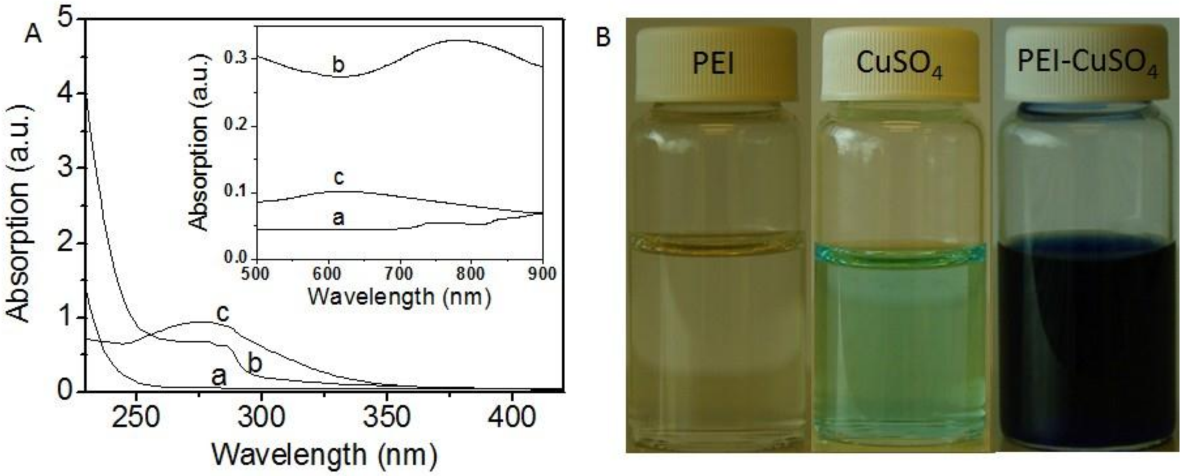

Figure S2 UV-Vis absorption spectra (A) and optical images (B) of PEI (a), $CuSO_4$ (b), and C_2H_5N-Cu complex networks (c).

Figure S2, A illustrate absorption spectra of PEI (a), $CuSO_4$ (b) and C_2H_5N-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_2H_5N-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 σ(N)→antibonding $d_{x^2-y^2}$(Cu) charge transfer.[6] These observations confirms formation of C_2H_5N-Cu complexes.

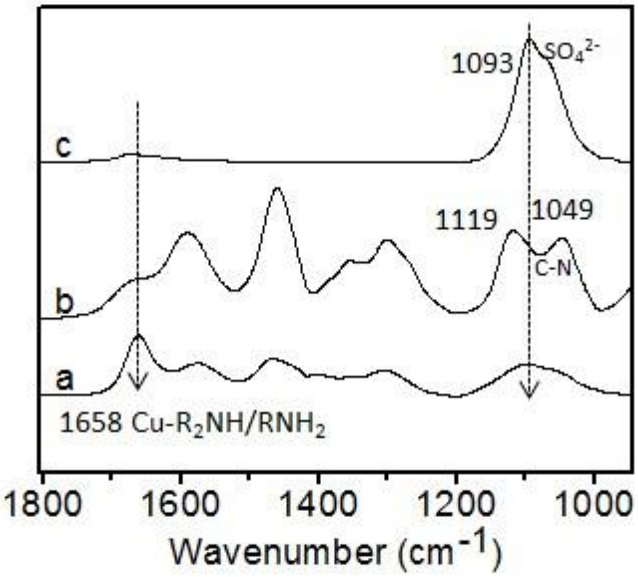

Figure S3 ATR-FTIR spectra of $CuSO_4$ (a), PEI (b) and C_2H_5N-Cu supramolecular polymer networks (c).

Figure S3 illustrates ATR-FTIR spectra of $CuSO_4$ (a), PEI (b) and C_2H_5N-Cu supramolecular polymer networks (c). The bands at 1093, 1049 and 1119 cm^{-1} in Trace a and b due to the streching 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_2H_5N-Cu complex formation. These observations confirm the formation of C_2H_5N-Cu complex networks.

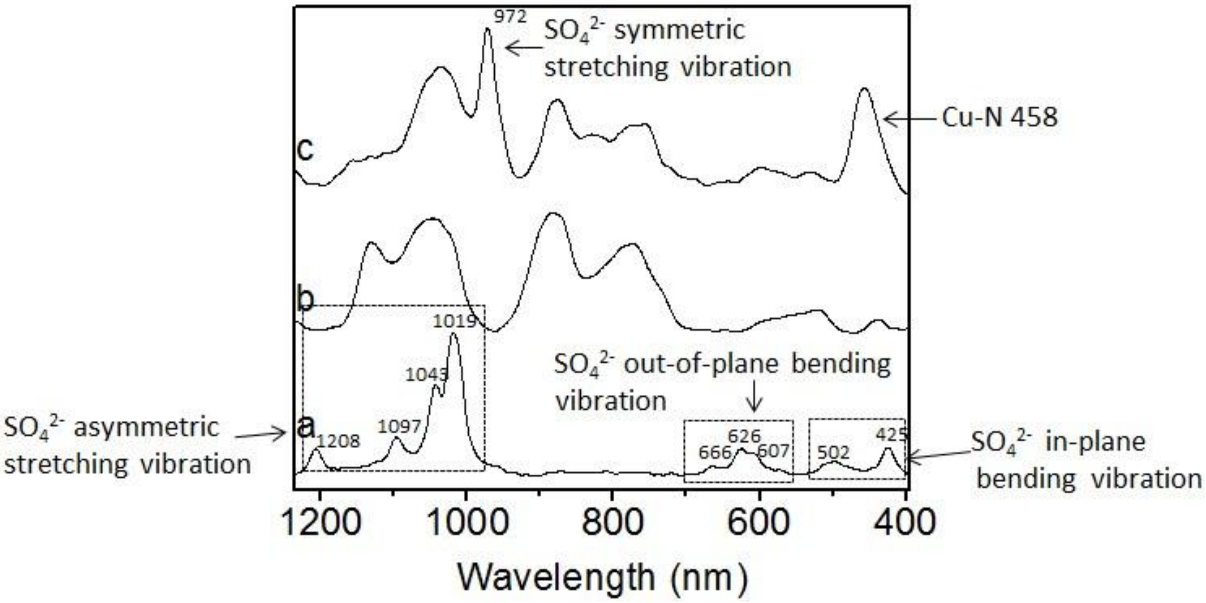

Figure S4 Raman spectra of $CuSO_4$ (a), PEI (b) and C_2H_5N-Cu supramolecular polymer networks (c).

Figure S4 shows Raman spectra of $CuSO_4$ (a), PEI (b) and C_2H_5N-Cu supramolecular polymer networks (c). $CuSO_4$ (trace a) exhibits asymmetric streching 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 C_2H_5N-Cu complexes are formed, only symmetic streching vibrations at 972 cm^{-1} corresponding to S-O are observed[4], indicating that all of Cu^{2+} 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.

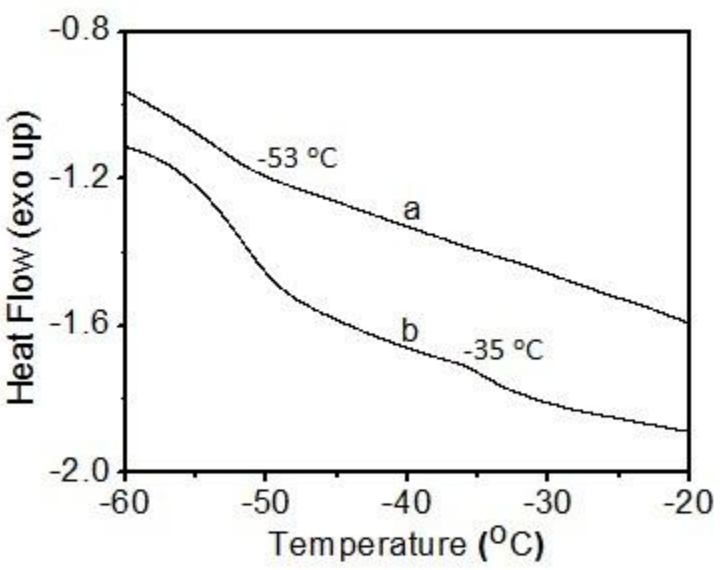

Figure S5 Modulated differential scanning calorimetry (MDSC) of PEI (a) and C_2H_5N-Cu supramolecular polymer networks (b).

Figure S5 illustrates modulated differential scanning calorimetry (MDSC) thermograms of PEI (a) and C_2H_5N-Cu supramolecular polymer networks (b). When $CuSO_4$ is added to PEI, Tg of PEI increases from -53 to -35 ^{o}C, thus indicating formation of the C_2H_5N-Cu supramolecular polymer network.

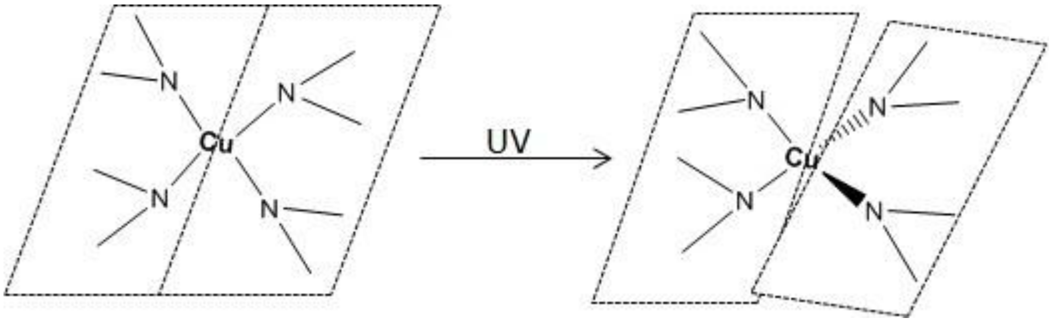

Figure S6 Square-planar and tetrahedral configurations for C_2H_5N-Cu complexes formed in C_2H_5N-Cu supramolecular polymer networks

Figure S6 shows two configurations of C_2H_5N-Cu complex. Upon UV exposure, the C_2H_5N-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].

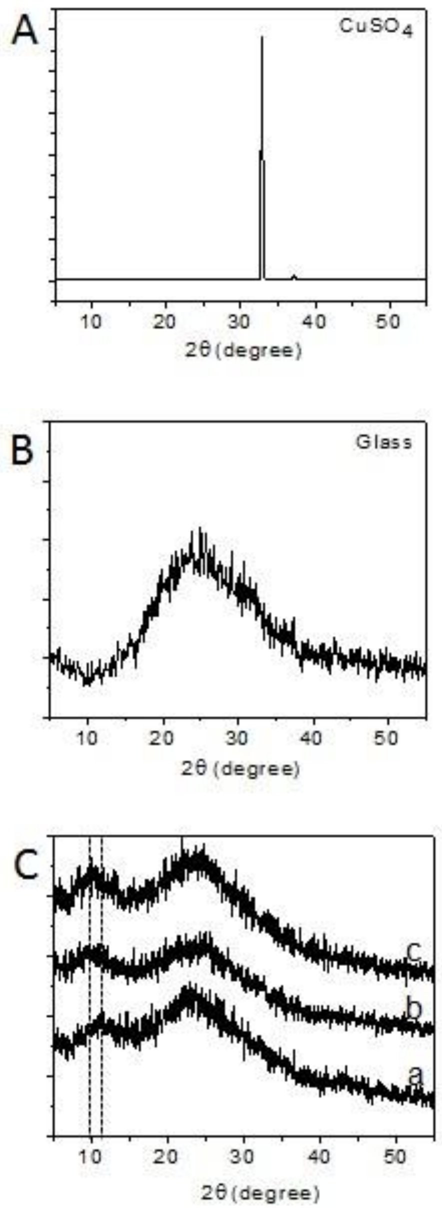

Figure S7 X-ray diffraction patterns of $CuSO_4$ (A), glass substrate (B) and damaged C_2H_5N-Cu supramolecular polymer networks (C) as a function of UV exposure. a) 0 h; b) 1 h; c) 3 h.

Figure S7, A and B, illustrate X-ray diffraction patterns of $CuSO_4$ and glass substrate, respectively. $CuSO_4$ exhibits a diffraction peak at $2\Theta = 32.8^{o}$, while glass substrate has a broad diffraction at $2\Theta = 24.6^{o}$. X-ray diffraction patterns of damaged C_2H_5N-Cu supramolecular networks as a function of UV exposure are shown in Fiugre 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 $2\Theta = 11.2^o$ confirm the formation of C_2H_5N-Cu supramolecular networks.[5] With the increased UV exposure, 2Θ at 11.2^o shifts to 10.1^o, 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 $11.2\ ^o$ peak shift towards lower angles[9] (Figure S7, C).

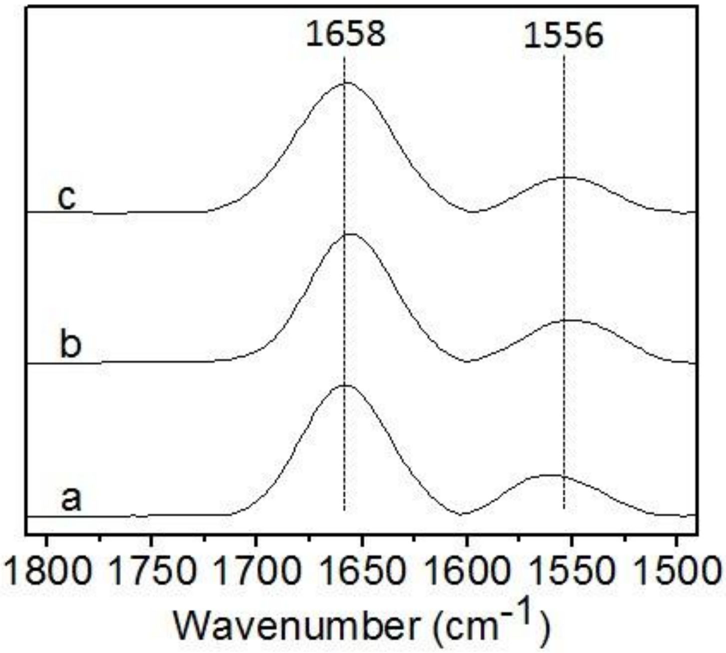

Figure S8 ATR-FTIR spectra of undamaged C_2H_5N-Cu supramolecular polymer networks as a function of UV exposure time: a) 0 h; b) 1 h; c) 3 h.

Figure S8 illustrates ATR-FTIR spectra of undamaged C_2H_5N-Cu supramolecular polymer networks as a function of UV exposure. With the increased UV exposure time, undamaged C_2H_5N-Cu networks show no spectral changes, indicating that only damaged areas are affected by UV exposure.

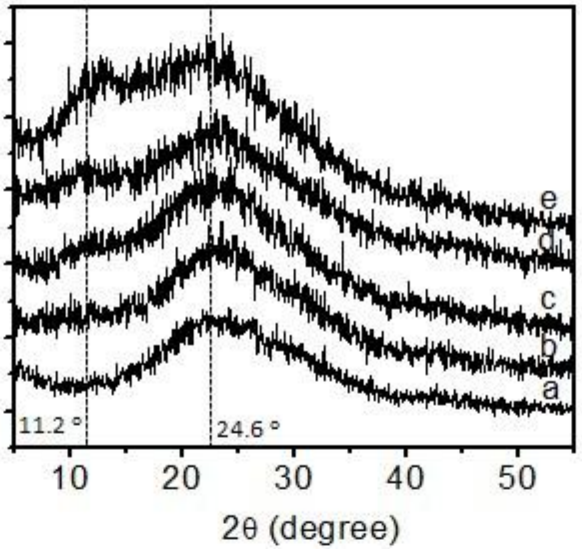

Figure S9 X-ray diffraction patterns of the C_2H_5N-Cu supramolecular polymer networks. a, C_2H_5N:Cu = 80; b, C_2H_5N:Cu = 60; c, C_2H_5N:Cu = 40; d, C_2H_5N:Cu = 30; e, C_2H_5N:Cu = 20.

Figure S9 shows X-Ray diffraction of C_2H_5N-Cu supramolecular polymer networks with the following C_2H_5N-Cu molar ratios: 80 (a), 60 (b), 40 (c), 30 (d), 20 (e). Intensity of the diffraction peaks at $2\Theta=11.2\ ^{o}$ increases with the decreased C_2H_5N-Cu molar ratio, demonstrating that more C_2H_5N-Cu complexes are formed at lower C_2H_5N-Cu molar ratio. Cross-linking degree of this C_2H_5N-Cu supramolecular polymer networks depends on the content of C_2H_5N-Cu coordination, therefore the network cross-linking density increases with the decreased C_2H_5N-Cu molar ratio.

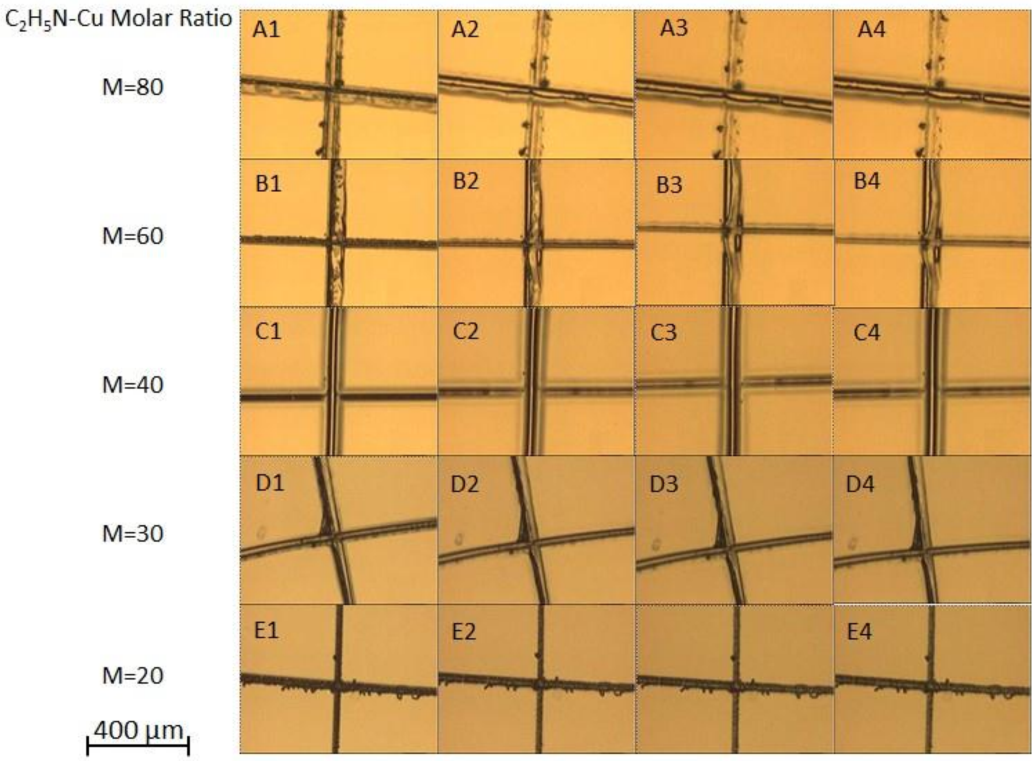

Figure S10 Optical images of mechanically damaged C_2H_5N-Cu supramolecular polymer networks. A1, A2, A3 and A4 are optical images heated at 50 ^{o}C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 80); B1, B2, B3 and B4 are optical images heated at 50 ^{o}C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 60); C1, C2, C3 and C4 are optical images heated at 50 ^{o}C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 40); D1, D2, D3 and D4 are optical images heated at 50 ^{o}C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 30); E1, E2, E3 and E4 are optical images heated at 50 ^{o}C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 20).

Figure S10 illustrates self-healing behavior of mechanically damaged C_2H_5N-Cu supramolecular polymer networks with the following C_2H_5N:Cu molar ratios at 50 ^{o}C: 80 (A1-A4), 60 (B1-B4), 40 (C1-C4), 30 (D1-D4), 20 (E1-E4). At this temperature, all of the C_2H_5N-Cu supramolecular polymer networks can not be repaired. Since the actual sample temperature is ~ 30 ^{o}C after UV exposure, the self-healing is not caused by heat but activiation of the Cu-N coordination bonds.

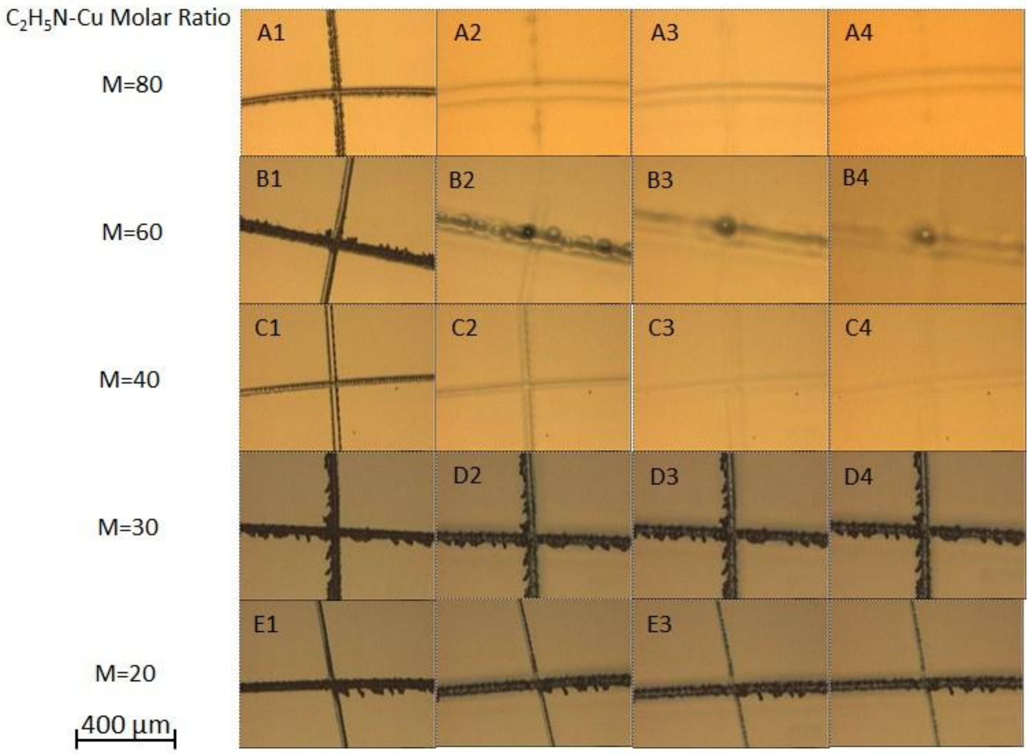

Figure S11 Optical images of mechanically damaged C_2H_5N-Cu supramolecular polymer networks. A1, A2, A3 and A4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 80); B1, B2, B3 and B4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 60); C1, C2, C3 and C4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 40); D1, D2, D3 and D4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 30); E1, E2, E3 and E4 are optical images heated at 75 °C for 0, 6, 24 and 48 hrs (C_2H_5N:Cu = 20).

Figure S11 illustrates self-healing behavior of the mechanically damaged C_2H_5N-Cu suparmolecular polymer networks with the following C_2H_5N: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_2H_5N-Cu molar ratio ≥ 40) can be repaired, which also identifies that the self-healing upon UV exposure is not caused by heat but activiation of the Cu-N coordination bonds.

References

1. a) T. D. Perrine, W. R. Landis, *J. Polym. Sci., Part A: Polym. Chem.* **1967,** *5,* 1993-2003. b) F. Ungaro, G. D. Rosa, A. Miro, F. Quaglia, *J. Pharm. Biomed. Anal.* **2003,** *31,* 143-149.

2. D. Michalska, K. Hernik, R. Wysokinski, B. Morzyk-Ociepa, A. Pietraszko, *Polyhedron* **2007,** *26,* 4303-4313.

3. R. L. Frost, *J Raman Spectroc,* **2011,** *42,* 1130-1134.

4. P. Drozdzewski, H. Zaslona, M. Kubiak, *Struct. Chem.,* **2010,** *21,* 405-414.

5. M. W. Urban, Attenuated Total Reflectance Spectroscopy of Polymers; Theory and Applications. *American Chemical Society and Oxford University Press*, Washington, DC, 1996.

6. Z. Koziskova, J. Gazo. *Chem Zvesti.* **1984**, *38,* 583.

7. I. Grenthe, P. Paoletti, M. Sandstrom, S. Glikberg. *Inorg. Chem.* **1979,** *18,* 2687.

8. K. Takahashi, R. Nakajima, Z. Gu, H. Yoshiki, A. Fujishima, O. Sato. *Chem Commun,* **2002,** *38,* 1578-1579.

9. P. Naumov, K. Sakurai. *Chem. Phys. Lett.* **2006**, *427,* 343-345.