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## **Supporting Online Materials**

## UV-Induced Self-Repairing Polydimethylsiloxane-Polyurethane (PDMS-PUR) Cu-

## **Catalyzed Networks**

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Figure S1. NMR spectra of PDMS

In order to determine the number of repeated units in PDMS, <sup>1</sup>H NMR spectra shown in Figure S1 were recoreded. The area ratios for <sup>a</sup>H and <sup>b</sup>H resonances was determined to be 4 : 61.72. The average molecular weight of PDMS was determined by ratioing a:b=4:61.72 and number of repeating units n=61.72÷6=10.3, giving  $M_n = 877.2$ .



Figure S2. NMR spectra of HDI

In order to determine the composition of the isocyanate, <sup>1</sup>H NMR spectrum was recorded shown in Figure S2. The area ratio of <sup>a</sup>H : <sup>b</sup>H : <sup>c</sup>H : <sup>d</sup>H = 2 : 2.75 : 2.75 : 1, indicating a 2:3 ratio of mono-HDI and tri-HDI in the composition with no presence of di-HDI.



Figure S3 ATR-IR spectra of: a -  $CuCl_2$ , b - PDMS, c - HDI, and d - PDMS-PUR-Cu $Cl_2$  networks.

Figure S3 illustrates ATR-IR spectra of CuCl<sub>2</sub> (a), PDMS (b), HDI (c) and PDMS-PUR-CuCl<sub>2</sub> networks (d). The bands at 1022 and 1080 cm<sup>-1</sup> due to asymmetric Si-O stretching and 1250 cm<sup>-1</sup> attributed to C-H symmetric deformations of Si-CH<sub>3</sub> group appear in trace b and c, demonstrating that PDMS is copolymerized into PDMS-PUR-CuCl<sub>2</sub> networks. The asymmetric stretching vibration at 2268 cm<sup>-1</sup> and symmetric stretching vibration at 1355 cm<sup>-1</sup> due to -N=C=O functionalities disappear in trace d, signifying all NCO groups have been reacted. These observations confirms that PUR-PDMS-CuCl<sub>2</sub> networks were successfully synthesized.



**Figure S4** Raman spectra of: a - CuCl<sub>2</sub>, b- CuCl<sub>2</sub> film deposited form DMF, c - PDMS-PUR-CuCl<sub>2</sub>, and d - PEG-PUR-CuCl<sub>2</sub> networks.

Figure S4 illustrates Raman spectra of CuCl<sub>2</sub> (a), CuCl<sub>2</sub> layers deposited form DMF (b), PDMS-PUR-CuCl<sub>2</sub> (c) and PEG-PUR-CuCl<sub>2</sub> networks (d). The band at 285 cm<sup>-1</sup> attributed to longitudinal vibrations of Cu-Cl bonds shifts to lower energy, thus suggesting the CuCl<sub>2</sub> oligomers formation. The band at 193 cm<sup>-1</sup> due to the transverse vibrations of Cu-Cl bonds is detected in the PDMS-PUR-CuCl<sub>2</sub> network (c), while the band at 285 cm<sup>-1</sup> diminishes to minimum, manifesting the formation of Cu-O coordination bond. Figure S5 A illustrates the formation of CuCl<sub>2</sub> oligomers, and Figure S5 B shows transverse and longitudinal vibrational modes of Cu-Cl bonds detected in Raman measurements.



**Figure S5** A - Schemetic representation of two structure of copper chloride. B - Transverse and longitudinal vibrational modes of Cu-Cl bonds.



**Figure S6** ATR-IR spectra of: a - PEG-PUR-DBTDL, b - PDMS-PUR-DBTDL, c - PEG-PUR-CuCl<sub>2</sub>, and d - PDMS-PUR-CuCl<sub>2</sub> networks.

Figure S6 illustrate ATR-IR spectra of PEG-PUR-DBTDL (a), PDMS-PUR-DBTDL (b), PEG-PUR-CuCl<sub>2</sub> (c) and PDMS-PUR-CuCl<sub>2</sub> (d) networks. The bands at 1097 and 1093 cm<sup>-1</sup> due to asymmetric vibrations of C-O-C entities in PEG are detected in Traces a and c, demonstrating PEG macromonomer incorpration into PEG-PUR network . The bands at 1080 cm<sup>-1</sup> and 1022 cm<sup>-1</sup> due to asymmetric vibrations of Si-O-Si in PDMS observed in Traces b and d demonstrate that PDMS was incorprated into PDMS-PUR network.



**Figure S7.** Raman spectra of PDMS-PUR networks in the 120-580, 620-670 and 2800-3500 cm<sup>-1</sup> regions collected from of undamaged (A1-A3) and damaged (B1-B3) areas as a function of UV exposure for 0 h (a), 0.5 h (b), and 2 h (c).



**Figure S8.** Raman spectra of PEG-PUR networks in the 200-600, 900-1200, and 1600-1900 cm<sup>-1</sup> regions collected from undamaged (A1-A3) and damaged (B1-B3) areas as a function of UV exposure for 0 (a), 0.5 (b), and 2 hrs (c).