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Hybrid polymer networks of carbene and thiol ene

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1	Hybrid polymer networks of carbene and thiol ene
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15	SUPPLEMENTARY INFORMATION
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- 22 <u>Supplementary video 1.</u> UVA activation of thiol/alkene/CaproGlu hybrid network.



- 25 <u>Supplementary video 2.</u> Sample cut for lap shear adhesion test and scratch test demonstration
- 26 after UVA activation of thiol/alkene/CaproGlu hybrid network.
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Figure S1. 3-component thiol/alkene/CaproGlu hybrid polymer network (SH1/Ene2/Dz;
Table 1) sample preparation for FTIR and SEM analysis: (A) sample fixed with needle
between 2 UVA diodes (100 mW.cm⁻²); (B) diodes turned ON simultaneously for 100 sec to
deliver 10 J.cm⁻² to each side of the sample; (C) sample after UVA curing.



Figure S2. Digital photographs of crosslinked 3-component thiol/alkene/CaproGlu hybrid
polymer network samples in ambient conditions 24 h after mixing (no UVA activation; bar =
1 cm): (A-C) SH2/Ene2/Dz, SH1/Ene2/Dz and SH1/Ene1.5/Dz (nomenclature and
composition: Table 1) respectively.



- Figure S3. Photographs of samples prepared for peel test: (A) SH1/Ene2 (no CaproGlu)
 control; (B-D) HPN samples with compositions outlined in Table 1.



Figure S4. Peel test experimental design for samples placed between 2 collagen sheets: (A)
Glass slide/cyanoacrylate/Collagen/HPN/Collagen structure fixed with paper clips after UVA
activation (20 J.cm⁻²: 10 J.cm⁻² from either side of the sample); (B) Collagen/HPN/Collagen
structure mounted on the sample holder for peel strength test.

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Figure S5. 1-step light-activated crosslinking of pure CaproGlu analyzed with photorheometry - dynamic change of storage (G') and loss (G'') moduli over time (bottom) and absorbed energy dose (top' J.cm⁻²) with indicated gelation point (G' = G'') upon light activation (diode wavelength range = 320-500 nm; diode power = 100 mW.cm⁻²).





Figure S6. Photorheological profiles of 3-component thiol/alkene/CaproGlu hybrid polymer
networks (Table 1) SH2/Ene2/Dz and SH1/Ene1.5/Dz (A and B respectfully) with dynamic
change of storage (G') and loss (G'') moduli upon 2-step light activation at 405 nm and 365
nm (light diode power: 100 mW.cm⁻²) over time (bottom) and absorbed energy dose (top; J.cm⁻
²).

- 83 **Table S1.** Dynamic (storage) modulus (G') of hybrid networks and controls recorded 1 min
- 84 after the light diodes are turned off (see **Fig. 3**; **Fig. S3**) and gelation points expressed as light 85 energy (I) dose required to reach G' = G'' value

85	energy (J) dose required to reach $G = G$	value.

Hybrid network composition	G' (405 nm; kPa)	G' (365 nm; kPa)	Gel. Point (J.cm ⁻²)	
CaproGlu (Control-1)	-	170	2	
SH/Yne (Control-2)*	-	5750 [*]	6	
SH2/Yne2/Dz*	-	500*	4	
SH/Ene (Control-3)	1520	1530	-	
SH2/Ene2/Dz	16	410	-	
SH1/Ene2/Dz	28	920	-	
SH1/Ene1.5/Dz	7	630	-	

^{*}*Measured upon 1-step activation at polychromatic light: 320-500 nm; 30 J.*

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Figure S7. Magnified region of normal force vs light activation time (405 nm; the full range is
displayed in Figure 3D in main text); the thiol-acrylate (SH-Ene) crosslinking causes polymer
volume shrinking as evident from drop in normal force, in comparison to pure CaproGlu
(control-1).

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Figure S8. Degree of alkene conversion (DC %) calculated from absorbance value at 810 cm⁻¹ normalized to carbonyl peak of PEGDA (Ene; 1721 cm^{-1}): (Left) FTIR representative spectral

98 region with data readings (R) used to calculate absorbances (A) normalized to carbonyl peaks;

99 (Right) DC (%) calculated for SH1/Ene2/Dz after mixing and exposure to ambient light for 24

100 h (mark as "Neat" – without UVA activation).



Figure S9. Peel strength vs displacement curves of CaproGlu (control; n = 3) and HPN (n = 3)
samples after activation with UVA light (20 J.cm⁻²): (A-C) CaproGlu; (D-F): SH2/Ene2/Dz.
Vertical lines indicate the peel strength data range used to calculate the average values for each
sample.



Figure S10. Peel strength vs displacement curves of HPN (n = 3) samples after activation with UVA light (20 J.cm⁻²): (A-C) SH1/Ene2/Dz; (D-F): SH1/Ene1.5/Dz. Vertical lines indicate the peel strength data range used to calculate the average values for each sample.



Figure S11. Peel strength vs displacement curves of HPN (n = 3) samples without UVA activation: (A-C) SH1/Ene2/Dz. Vertical lines indicate the peel strength data range used to calculate the average values for each sample.

121 Table S2. 3-component thiol/alkene/CaproGlu hybrid network SH1/Ene2/Dz (Table 1)

122 composition – 7 samples measured prior to UVA activation and lap shear adhesion experiment;

123	the density is calculated	rom sample weight a	nd dimensions:	$\rho = (1.1 \pm 0.1) \text{ g.cm}^{-3}.$
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Sample	Length (cm)	Width (cm)	Thicknes (cm)	Weight (g)	Volume (cm ⁻³)	ρ (g.cm ⁻³)
1	0.7	0.6	0.15	0.0623	0.06	0.99
2	0.7	0.6	0.15	0.0635	0.06	1.01
3	0.65	0.6	0.17	0.0745	0.07	1.12
4	0.65	0.6	0.2	0.0817	0.08	1.05
5	0.7	0.6	0.2	0.1054	0.08	1.25
6	0.65	0.5	0.2	0.0891	0.07	1.37
7	0.65	0.5	0.2	0.072	0.07	1.11



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Figure S12. Lap shear adhesion test and representative mechanical profile of 3-component 132 thiol/ene/CaproGlu hybrid network - SH1/Ene2/Dz (n = 7): (A) experimental design for 133 crosslinking of SH1/Ene2/Dz sample in PMMA/hybrid network/PET sandwich structure by 134 crosslinking the network from 2 sides through light-transparent substrates (PMMA-bottom; 135 PET-top) by using 2 UVA diodes - each side of SH1/Ene2/Dz sample absorbed the UVE 136 energy = 10 J.cm^{-2} (total absorbed dose = 20 J.cm^{-2}); (B) representative lap shear adhesion 137 stress vs strain data recorded for SH1/Ene2/Dz (inset showing cohesive failure of SH1/Ene2/Dz 138 139 at yield point); (C) modulus vs strain with indicated maximum value at 197 kPa (dashed arrow indicates the modulus drop to initial value at 140 kPa); (D) modulus of toughness calculated as 140 area under stress vs strain curves (n = 7; individual curves for each measured sample are shown 141 in Supporting Information; ANOVA; interquartile range (IQR): 25th to the 75th percentile). 142





Figure S13. Lap shear adhesion stress vs strain profile measured for PMMA-hybrid network
(SH1/Ene2/Dz)-PET sandwich structure: (A) data collected for 7 samples and average value of
ultimate adhesion strength for SH1/Ene2/Dz; (B) pure CaproGlu (CG; control-1) data collected
from 6 samples measuring lap shear adhesion stress vs strain PMMA-CaproGlu-PET structure
and average value of ultimate adhesion strength; (C) photography of measured samples after
mechanical lap shear failure demonstrating cohesive adhesion.