Supporting information for

Tailoring Fully Biobased Optical Adhesives via Hydrogen-Bonding Modulation

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Materials

1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC HCl, ABCR 98%), sodium bicarbonate (Carl Roth, ≥ 99%), sodium sulfate (Carl Roth, ≥ 99%), hydrochloric acid (Chem-lab, 36%), chloroform-d (Eurisotop, 99.8%), anhydrous dichloromethane (DCM, Fischer Chemical, 99.8%), N,N-dimethylformamide (DMF, Fischer Chemical), 4-dimethylaminopyridine (DMAP, Fluorochem, 99%), and glycerol 1,2-carbonate (GCC, TCI-chemicals, > 90%) were used as received. Pripol 2033 and Priamine 1074 were kindly provided by Cargill. DL-α-lipoic acid was purchased from BulkSupplements.com and used as received.

Methods

Ester adhesive synthesis

Pripol 2033 (6 g, 11.17 mmol, 1 equiv.), DL-α-lipoic acid (LA, 4.61 g, 22.35 mmol, 2 equiv.), and 4-dimethyl amino pyridine (DMAP, 273 mg, 2.23 mmol, 0.2 equiv.) were dissolved in 100 mL anhydrous dichloromethane (DCM) in a dry and dark 250 mL two-neck round bottom flask. The solution was placed in an ice bath and cooled to 0°C after which 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC HCl, 6.43 g, 33.53 mmol. 3 equiv.) was added in portions under continuous stirring. After reaction completion, the mixture was extracted with 1N HCl (200 mL, three times), saturated sodium bicarbonate solution (200 mL, three times) and washed with brine (100 mL, three times). Finally, the organic phase was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to yield the title compound. Yield = 75% (viscous yellow liquid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.00-4.10 (t, 4H; COO-*CH_2*), 3.60-3.52 (m, 2H, S-*CH* dithiolane proton), 3.21-3.06 (m, 4H, S-*CH_2* dithiolane proton), 0.91-0.80 (m, 6H, CH_3 alkyl chain end proton).

Amide adhesive synthesis

A procedure similar to the ester adhesive synthesis was followed. Priamine 1074 (6 g, 10.97 mmol, 1 equiv.) was dissolved with LA (4.53 g, 21.94 mmol, 2 equiv.), and DMAP (268 mg, 2.19 mmol, 0.2 equiv.) in 100 mL of anhydrous DCM in a in a dry and dark 250 mL two-neck round bottom flask. The solution was placed in an ice bath and cooled to 0°C after which EDC HCl (6.31 g, 32.91 mmol, 3 equiv.) was added in portions under continuous stirring. After completion of the reaction, the mixture was extracted with 1N HCl (100 mL, three times), saturated sodium bicarbonate solution (100 mL, three times) and washed with brine (100 mL, three times). Finally, the organic phase was dried over anhydrous sodium sulfate, and the solvent was removed *in vacuo* to yield the title compound. Yield = 82% (viscous yellow liquid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.65-3.55 (m, 2H, S-*CH* dithiolane proton), 3.28-3.20 (q, 4H; NH-*CH_2*), 3.20-3.06 (m, 4H, S-*CH_2* dithiolane proton), 0.92-0.80 (m, 6H, CH_3 alkyl chain end proton).

LA-GCC synthesis

Glycerol 1,2-carbonate (GCC, 7.5 g, 63.51 mmol, 1 equiv.) was dissolved with LA (13.10 g, 63.51 mmol, 1 equiv.) and DMAP (0.3 equiv.) in 100 mL of anhydrous DCM in a dry and dark 250 mL two-neck round bottom flask. The solution was placed in an ice bath and cooled to 0°C after which EDC HCl (18.26g, 95.27 mmol, 1.5 equiv.) was added in portions under continuous stirring. After reaction completion, the mixture was extracted with 1N HCl (100 mL, three times), saturated sodium bicarbonate solution (100 mL, three times) and brine (100 mL, three times) and dried over anhydrous sodium sulfate. The solvent was then removed *in vacuo* to obtain the LA-GCC product. Yield = 86% (viscous yellow liquid)

^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.99-4.92 (m, 1H, CH cyclic carbonate proton), 4.62-4.56 (t, 1H, COO-CH_2 cyclic carbonate proton), 4.45-4.25 (m, 3H, COO-CH_2 cyclic carbonate proton and CH-CH_2-O cyclic carbonate proton), 3.65-3.55 (m, 1H, S-*CH* dithiolane proton).

Urethane adhesive synthesis

LA-GCC (7 g, 22.85 mmol, 2 equiv.) and Priamine 1074 (6.25 g, 11.42 mmol, 1 equiv.) were dissolved in 25 mL N,N-dimethylformamide (DMF) in a 50 mL round bottom flask and heated to 75°C under inert gas flow to avoid the amine carbonation during the synthesis. After 48 hours, the mixture was extracted with 1N HCl (25 mL, three times), saturated sodium bicarbonate solution (25 mL, three times) and washed with brine (25 mL, three times) and the product was purified by column chromatography (EtOAc/n-pentane, 1:3). The resulting fractions were dried with sodium sulfate and concentrated under reduced pressure. Yield = 44% (viscous orange liquid).

^{1}H NMR (400 MHz, $CDCL_3$, δ): 4.38-4.00 (m, 8H, COO-CH_2), 3.64-3.54 (m, 2H, S-*CH* dithiolane proton), 3.29-3.09 (m, 4H, S-CH_2 dithiolane proton and NH-CH_2), 0.95-0.81 (m, 6H, CH_3 alkyl chain end proton).

Nuclear Magnetic Resonance (NMR) spectroscopy

NMR spectra were recorded on a Bruker Ascend 400 (400 MHz) FT-NMR spectrometer at 25 °C in $CDCl_3$. Chemical shifts (δ) are expressed in parts per million (ppm) whereby the residual solvent peak (^{1}H = 7.26 ppm, ^{13}C = 77.16) served as an internal standard. Coupling constants (J) are reported in Hertz (Hz). The resonance multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintet), sext (sextet) or m (multiplet).

In situ shear oscillatory rheology

A TA Instruments DHR-3 rheometer was fitted with a quartz curing stage to enable photoirradiation of adhesive resins during measurement. 1.25 µL of adhesive was pipetted onto the quartz, corresponding to a sample heigh of 25 µm when used with an 8 mm parallel plate geometry. 50 mW/cm^2 365 nm light was delivered to the sample after 30 seconds of baseline measurement. A strain of 1% and a frequency of 1 rad/s were used.

Sample preparation for all material characterization

Samples were prepared by irradiating resins between Rain-X coated glass slides with 50 µm spacers. All samples were irradiated with 50 mW/cm^2 365 nm light for 2.5 minutes per side. This procedure was used for all subsequent samples unless otherwise noted.

UV/Vis absorption measurements

Adhesive extinction coefficients were measured using UV/Vis spectroscopy (Thermo Fisher Scientific Evolution 300) at wavelengths from 300–700 nm with data intervals of 1 nm through quartz cuvettes with a path length of 1 cm. Due to solubility constraints, the ester and amide adhesives were dissolved in toluene and the urethane adhesive was dissolved in methanol. Molar extinction coefficients were calculated using Beer's Law. Film % transmittance was measured using the same instrument through a 50 μm thick film over a range from 300–950 nm.

FTIR measurements

Measurements were recorded on a Perkin Elmer FTIR SPECTRUM 1000 spectrometer with a PIKE Miracle attenuated total reflection (ATR) unit in a frequency range from 4000 to 600 cm-1. Infrared spectra at elevated temperature were acquired on a Perkin Elmer FTIR SPECTRUM One spectrometer with ATR with a PIKE GladiATR ATR unit and a PIKE Technologies high-temperature control equipment in a frequency range from 4000 to 600 cm-1, starting from 20 °C to 170 °C (+10°C temperature interval) and spectra were recorded after 10 minutes at each temperature. For measurement of hydrogen bond strength at the various temperatures, C=O stretch centroid was calculated with equation 1:

Eqn 1: $\frac{\sum \tilde{\nu} * A}{\sum \tilde{\nu}}$

Dynamic mechanical analysis (DMA)

Films were prepared as stated above. DMA was performed using a TA instruments RSA-2 with the samples held in tension clamps. Samples were ramped from -80°C to 80°C at 3°C/min. A strain of 0.03% and a frequency of 1 Hz were used. T_g was calculated as the maximum of the tan δ peak and the breadth of the T_g was calculated with the FWHM.

Differential scanning calorimetry (DSC)

Films were prepared as stated above. DSC was run on a TA Instruments Discovery DSC 2500 with approximately 5 mg of material in a hermetic sample pan. Samples were ramped from –80 to 150°C at 5°C/min. with a heat cool heat cycle. Normalized second heating cycles are plotted, with the midpoint used for the T_g location and the endset–onset used for the breadth.

Swelling measurements

Films were prepared as stated above. Samples of approximately 10 mg were swelled in 2 mL solvent (toluene, acetone, methanol, and DI water) for 24 hours. After swelling, the samples were patted dry with a kimwipe and massed, with swelling ratio calculated by equation 2:

Eqn 2: $Q_v = \frac{swollen\ mass}{dry\ mass}$

Three replicates for each sample were measured, with average and standard deviation calculated.

Swelling measurements

Films were prepared as stated above. Samples of approximately 10 mg were swelled in 2 mL acetone for 24 hours. After swelling, the solvent was removed by decanting, followed by removal *in vacuuo* for 24 hours. Gel fraction was calculated by equation 3:

Eqn 3: $Gel\ fraction = \frac{extracted\ dry\ mass}{initial\ dry\ mass}$

Three replicates for each sample were measured, with average and standard deviation calculated.

Lap shear testing

Samples were prepared on either half glass slides (15.6 mm x 12.5 mm x 1mm) or on plasma-treated PET substrates (125 µm thick, ~12.7 mm wide). One side of each substrate was coated using a blade coater to achieve a film thickness of 50 µm. For glass slide samples, two paper clips were placed on either side of the substrate to apply uniform pressure and minimize bubble formation. PET samples were enclosed between two clean glass slides and secured with two paper clips to maintain consistent pressure. Cured samples were maintained in an aspect ratio of about 2:1 between substrates to maintain consistent failure modes. Shear measurements were performed on a TA.XT Texture Analyzer with a 50 kg load cell. The samples were placed into tension clamps and separated at a velocity of 1 mm/s until total separation of the bonded region was achieved. The lap shear strength and strain to break were reported from the resulting force-displacement curves, with the total force normalized by the area of the bonded samples.

Refractive index measurements

Samples were prepared on 25 µm thick PET substrates and blade coated to a film thickness of 50 µm. Samples were cured open face under 365 nm light at 50 mW/cm² for 5 minutes. The refractive index was measured using a Metricon prism coupler at three wavelengths: 636.6 nm, 524.7 nm, and 404.7 nm. The refractive index at 589 nm was then interpolated using a Cauchy curve fit. The transverse electric (TE) and transverse magnetic (TM) modes were measured, and the subsequent Cauchy curves were subtracted from one another to calculate the birefringence across the visible spectrum. Refractive index values reported are for the TE mode.

Haze measurements

Glass slides were cleaned with acetone and dried under compressed air. A small drop of each sample was deposited onto the slide with 50 µm spacers at the end of each slide. Two binder clips were used to maintain uniform pressure during curing. Samples were cured under 365 nm light at 50 mW/cm² for 2.5 minutes per side. Haze was measured in accordance with the ASTM D1003 standard using a Haze-Gard i instrument from BYK, with a measurement aperture of 4 mm. Haze measurements were taken at three different locations across each sample, and the average value and standard deviation were calculated.

Contact angle measurements

Glass slides and PET films were prepared as previously described. 5 µL of deionized water was added to the slide or film, and the droplet was photographed with a Canon EOS Rebel T7. The contact angle was fit using the software FIJI.

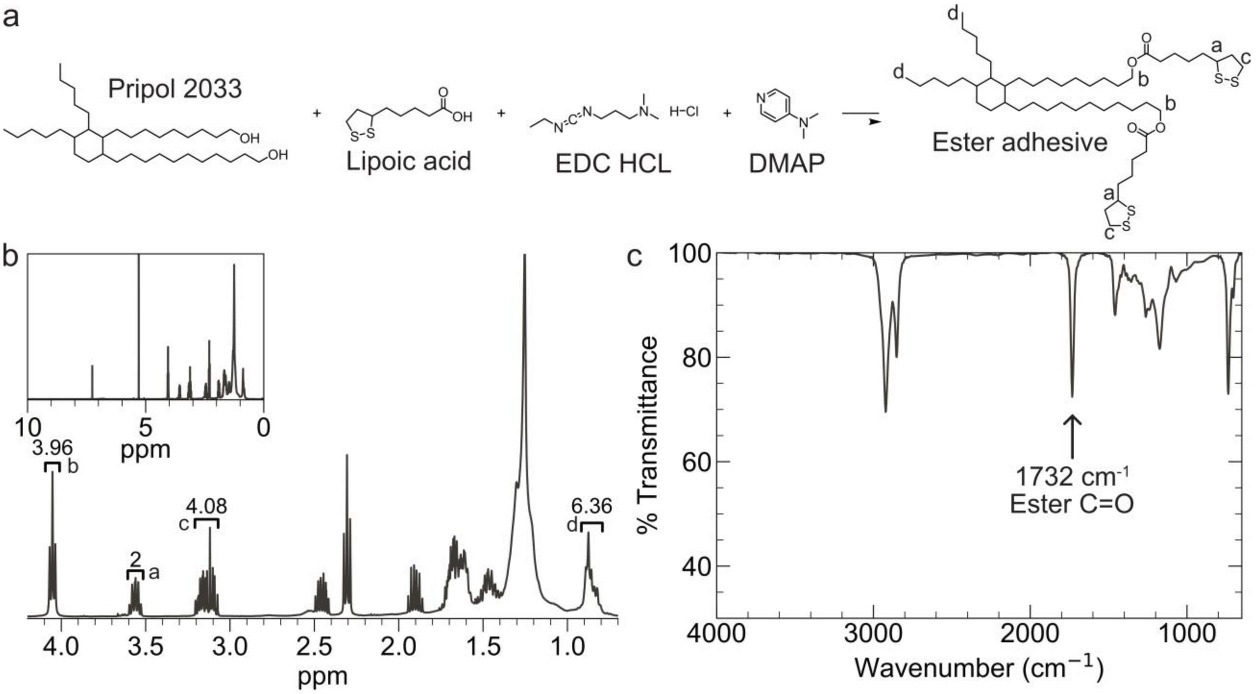

Figure S1. Ester adhesive monomer synthesis. (a) Synthesis scheme, through a Steglich esterification. (b) ^{1}H NMR (400 MHz, $CDCl_3$) of ester adhesive. Inset shows the full spectrum. Labeled protons are δ: b 4.00-4.10 (t, 4H; COO-*CH_2*), a 3.60-3.52 (m, 2H, S-*CH* dithiolane proton), c 3.21-3.06 (m, 4H, S-*CH_2* dithiolane proton), d 0.91-0.80 (m, 6H, CH_3 alkyl chain end proton). (c) FTIR of ester adhesive monomer. C=O stretch at 1732 cm^{-1} labeled.

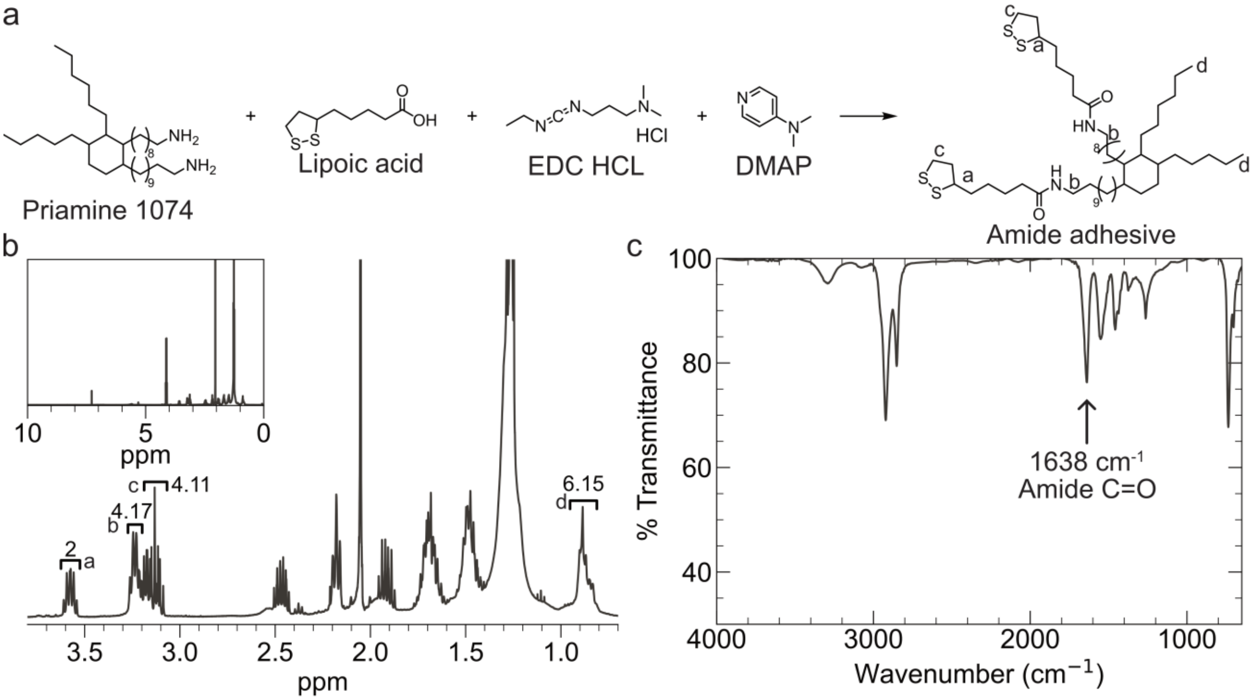

Figure S2. Amide adhesive monomer synthesis. (a) Synthesis scheme, through a Steglich amidation. (b) ^{1}H NMR (400 MHz, $CDCl_3$) of amide adhesive. Inset shows the full spectrum.

Labeled protons are δ: a 3.65-3.55 (m, 2H, S-*CH* dithiolane proton), b 3.28-3.20 (q, 4H; NH-CH_2), c 3.20-3.06 (m, 4H, S-CH_2 dithiolane proton), d 0.92-0.80 (m, 6H, CH_3 alkyl chain end proton). (c) FTIR of ester adhesive monomer. C=O stretch at 1638 cm^{-1} labeled.

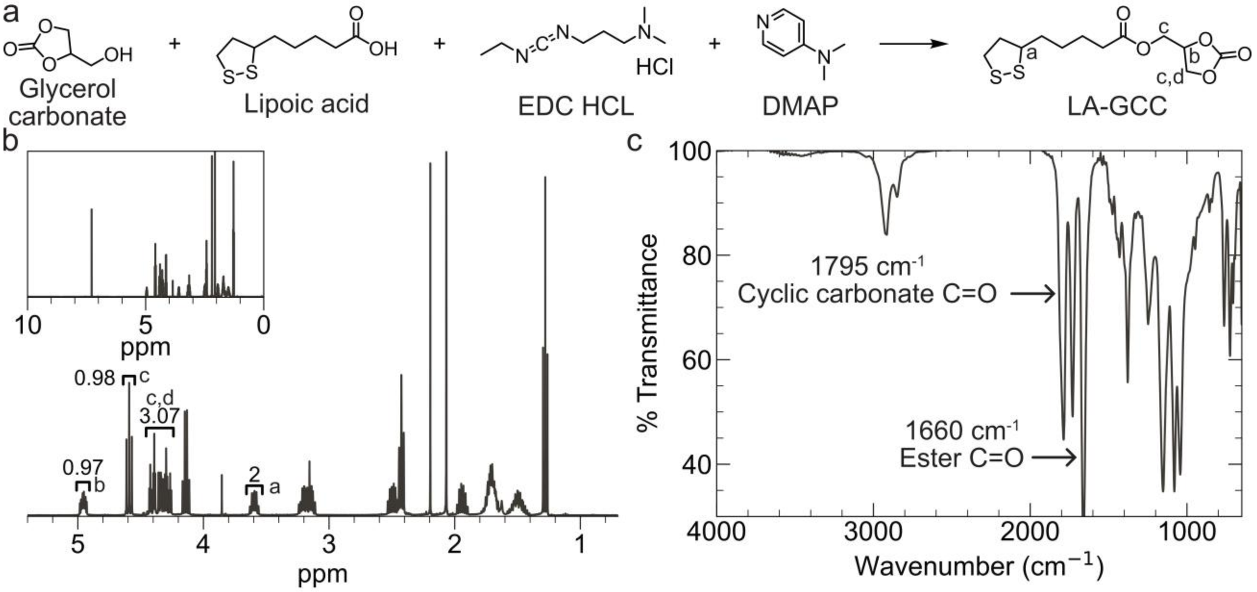

Figure S3. LA-GCC synthesis. (a) Synthesis scheme, through a Steglich esterification. (b) ^{1}H NMR (400 MHz, $CDCl_3$) of LA-GCC. Inset shows the full spectrum. Labeled protons are δ: b 4.99-4.92 (m, 1H, CH cyclic carbonate proton), c 4.62-4.56 (t, 1H, COO-CH_2 cyclic carbonate proton), c,d 4.45-4.25 (m, 3H, COO-CH_2 cyclic carbonate proton and CH-CH_2-O cyclic carbonate proton), a 3.65-3.55 (m, 1H, S-*CH* dithiolane proton). (c) FTIR of LA-GCC. C=O stretch at 1638 cm^{-1} labeled.

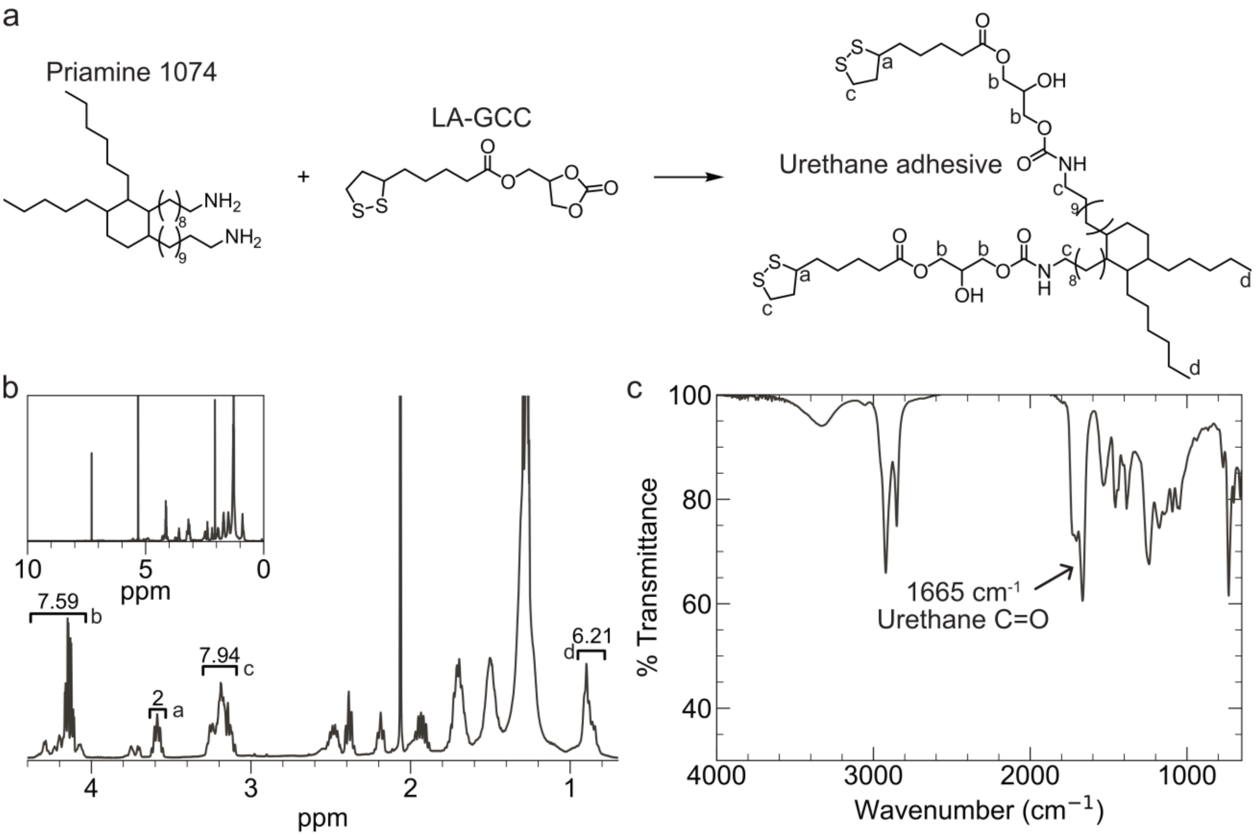

Figure S4. Urethane adhesive monomer synthesis. (a) Synthesis scheme, reacting the cyclic carbonate with the amine ta 75°C in DMF under inert atmosphere. (b) ^{1}H NMR (400 MHz, CDCl$_3$) of amide adhesive. Inset shows the full spectrum. Labeled protons are δ: b 4.38-4.00 (m, 8H, COO-*CH$_2$*), a 3.64-3.54 (m, 2H, S-*CH* dithiolane proton), c 3.29-3.09 (m, 4H, S-*CH$_2$* dithiolane proton and NH-*CH$_2$*), d 0.95-0.81 (m, 6H, CH$_3$ alkyl chain end proton). (c) FTIR of urethane adhesive monomer. C=O stretch at 1638 cm^{-1} labeled.

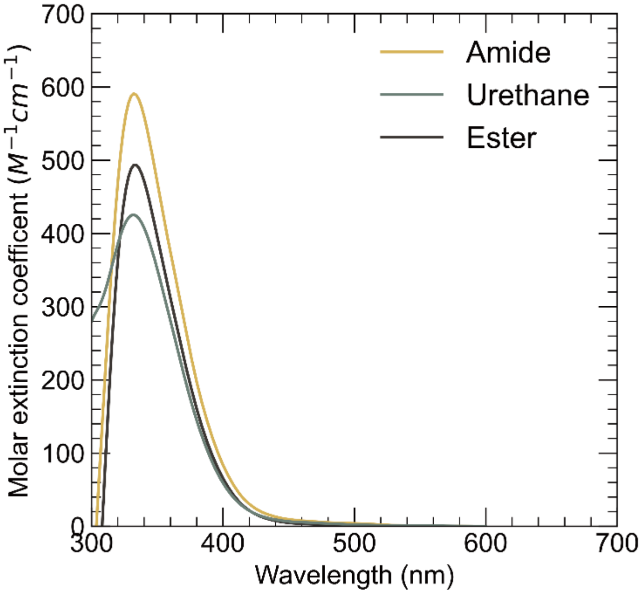

Figure S5. Molar extinction coefficient of adhesive precursors as a function of wavelength. Due to solubility constraints, the ester and amide adhesives were dissolved in toluene and the urethane adhesive was dissolved in methanol. Molar extinction coefficients were calculated using Beer's Law.

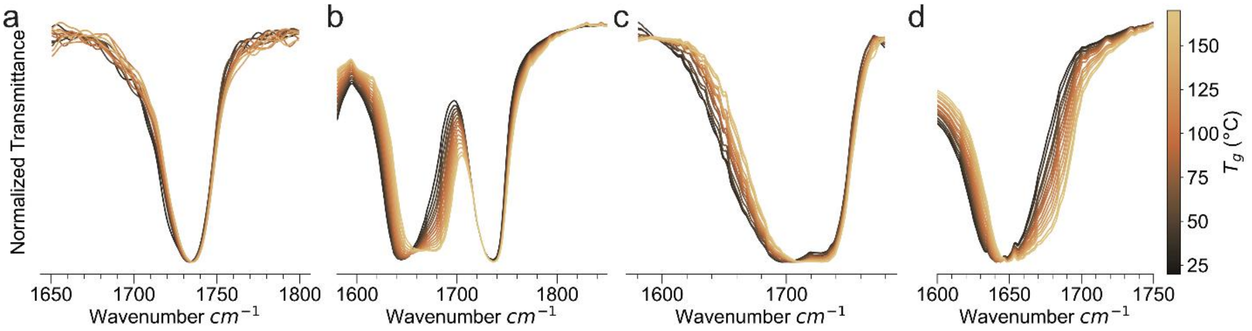

Figure S6. FTIR of C=O stretch for each adhesive sample at variable temperature. Transmittance normalized to the peak region for a) ester, b) mixture, c) urethane, and d) amide samples. Colorbar at right shows temperature corresponding to each spectrum from 20 to 170°C. FTIR taken on polymerized films.

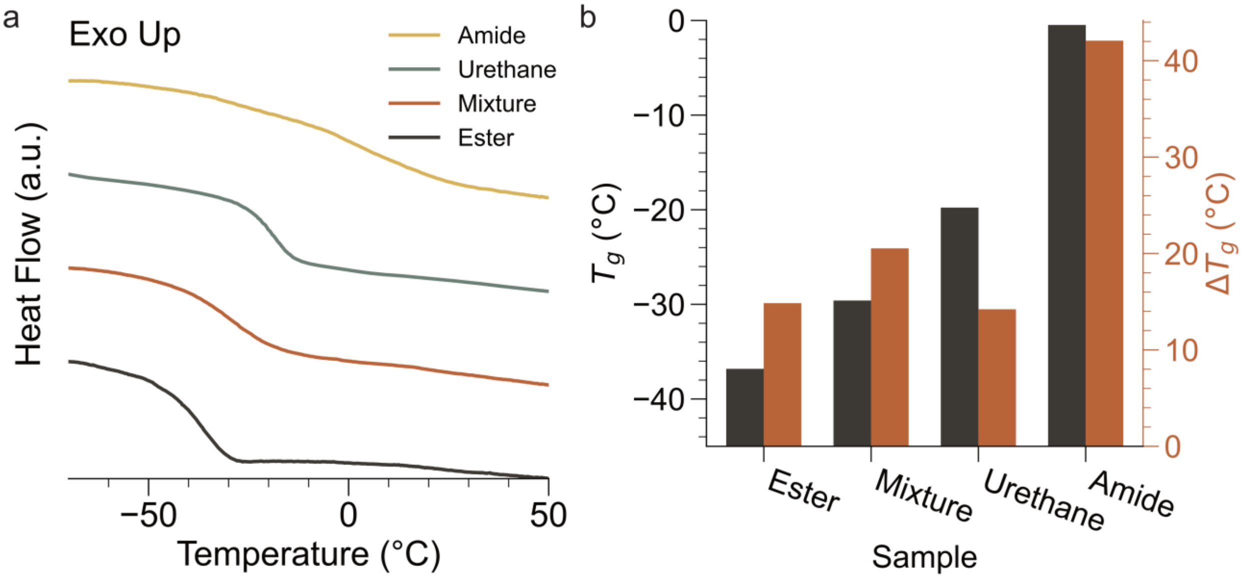

Figure S7. DSC of dithiolane adhesives. (a) Second heating traces highlighting the T_g in photocrosslinked films (exo up). (b) Glass transition temperature and endset-onset breadth as calculated from the DSC in (g).

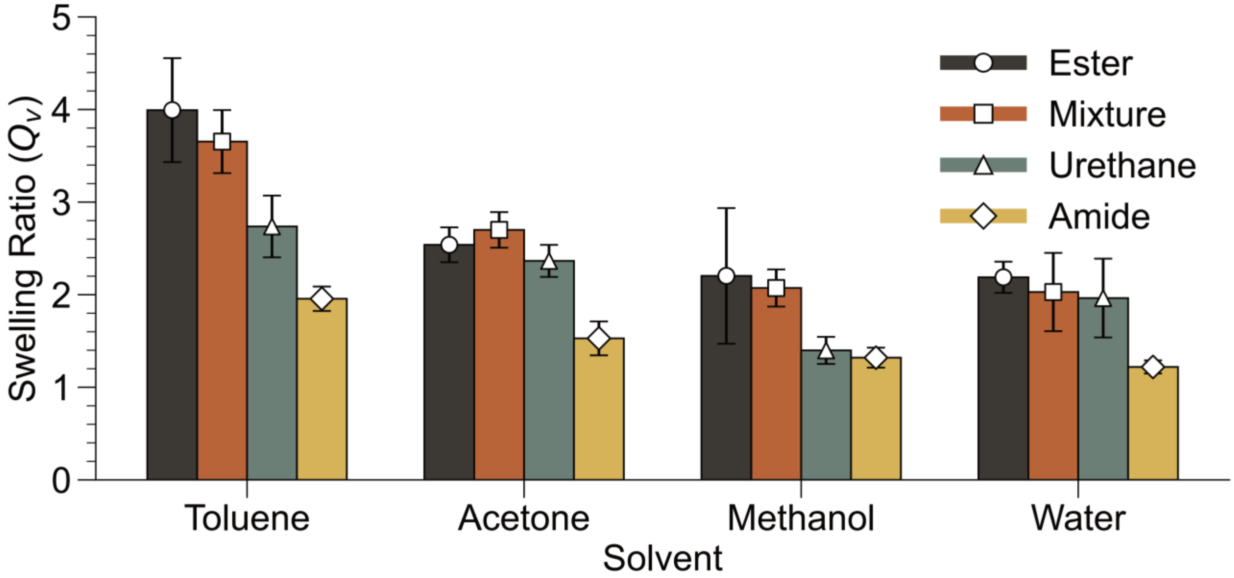

Figure S8. Swelling ratio of films in various solvents (toluene, acetone, methanol, and water). Three replicates per sample with standard deviation reported as errors.

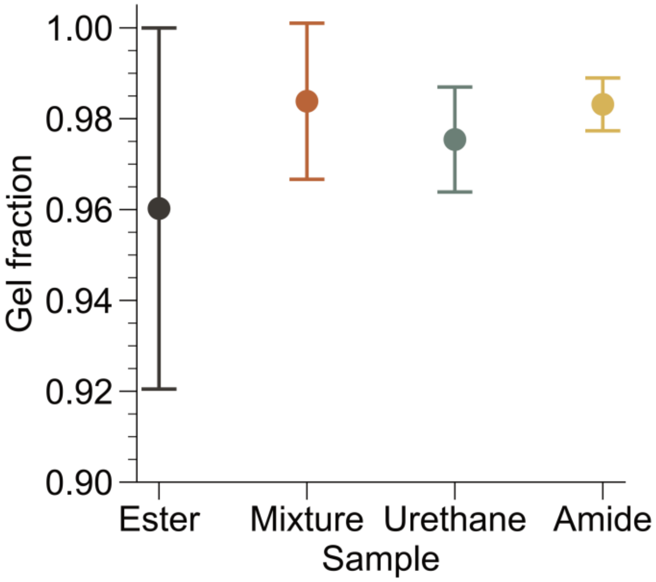

Figure S9. Gel fraction of films after swelling in acetone. Dried mass obtained after solvent removal and drying under vacuum. Three replicates per sample with standard deviation reported as errors.

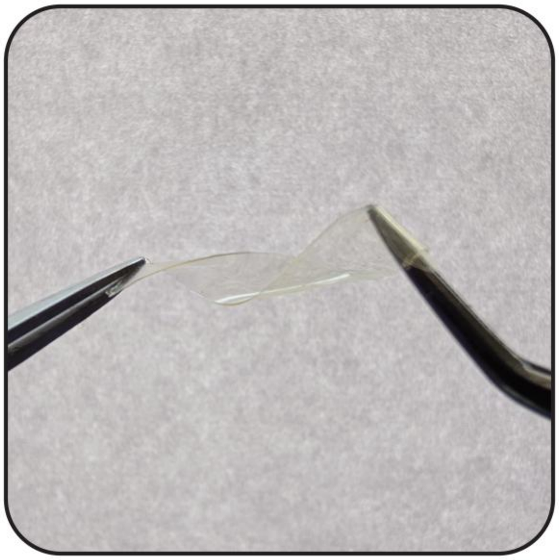

Figure S10. 50 µm thick amide film (approx. 0.5 cm x 5 cm) twisted with tweezers to demonstrate flexibility.

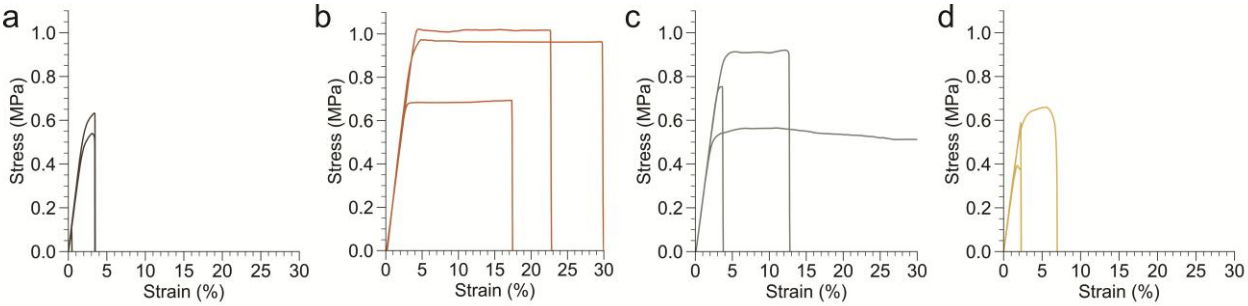

Figure S11. Lap shear testing on glass substrates. Lap joint formed between glass substrates using a) ester, b) mixture, c) urethane, and d) amide adhesives.

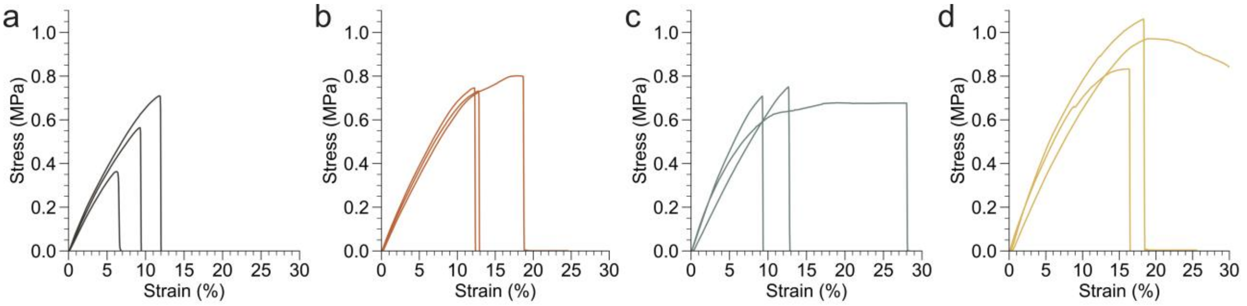

Figure S12. Lap shear testing on PET substrates. Lap joint formed between plasma coated PET substrates using a) ester, b) mixture, c) urethane, and d) amide adhesives.

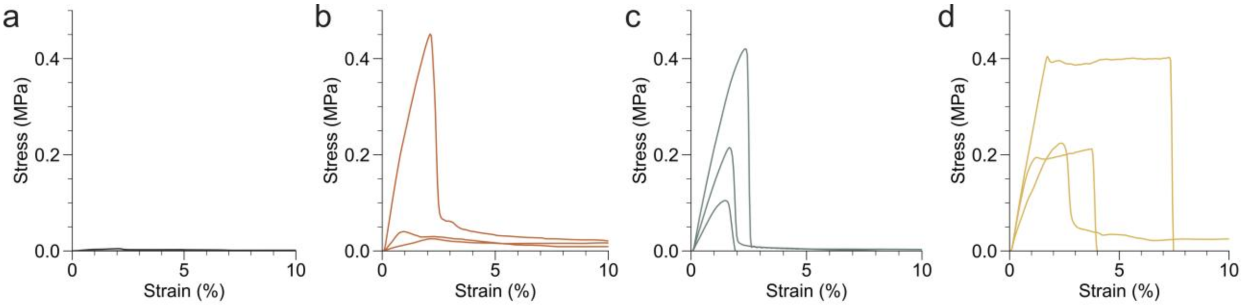

Figure S13. Lap shear testing on PMMA substrates. Lap joint formed between plasma coated PET substrates using a) ester, b) mixture, c) urethane, and d) amide adhesives. Only two replicates possible on ester sample due to failure.

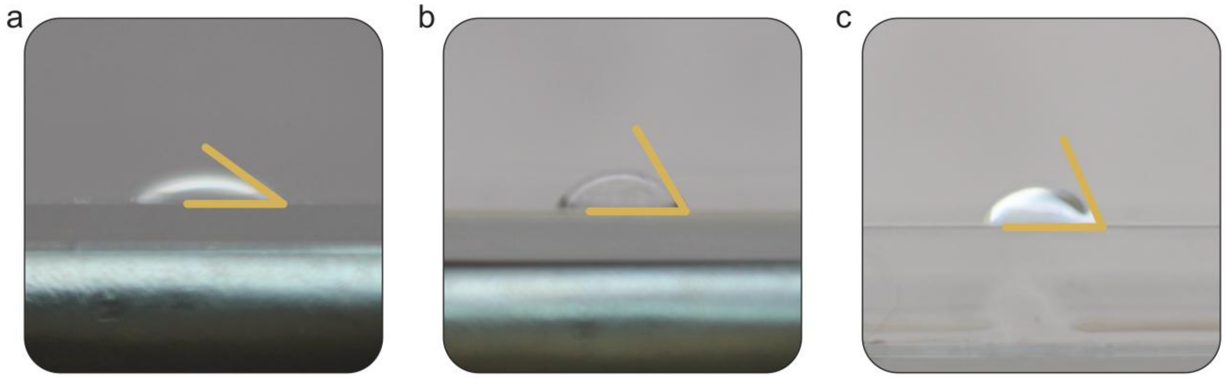

Figure S14. Contact angle measurements with water on (a) glass (36°) and (b) plasma treated PET (59°) and (c) PMMA (66°).

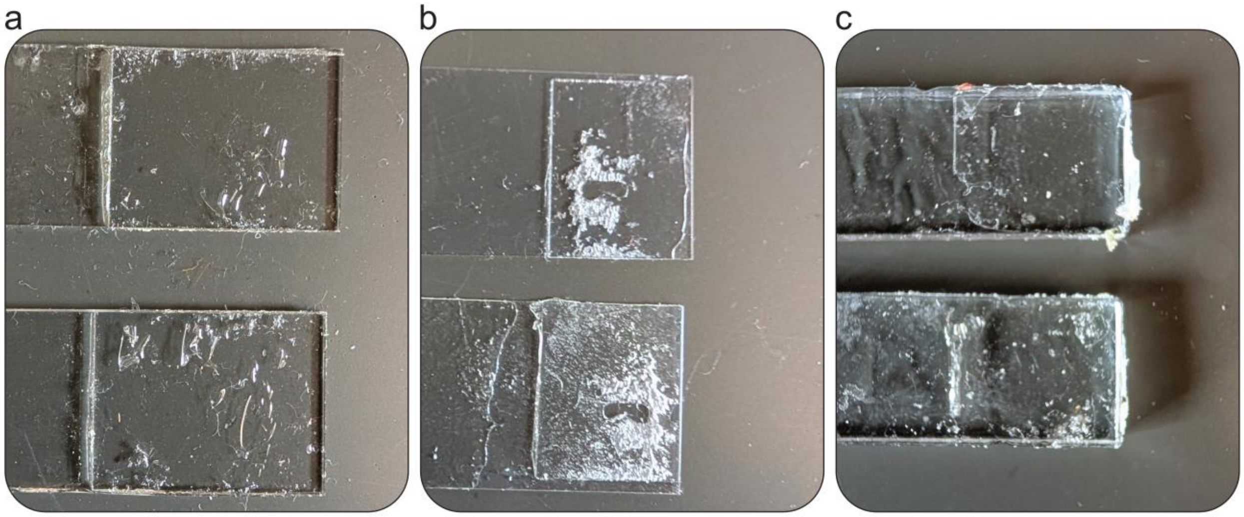

Figure S15. Failure modes in lap shear samples. (a) Adhesive failure in glass sample. (b) Cohesive failure in PET sample. (c) Cohesive failure in PMMA sample.

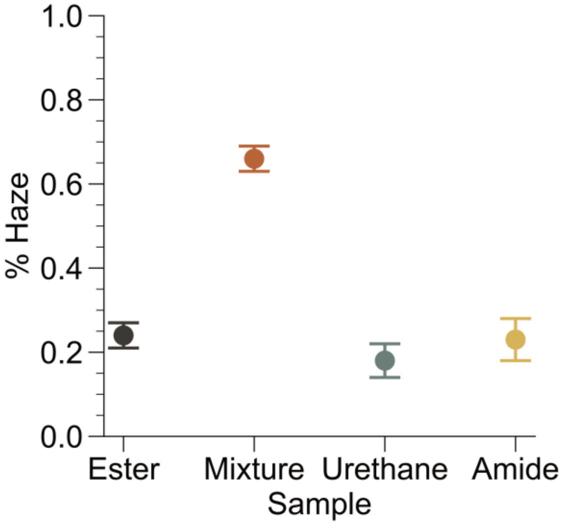

Figure S16. Haze of each sample measured when cured between glass slides. Haze measured according to the ASTM D1003 standard.

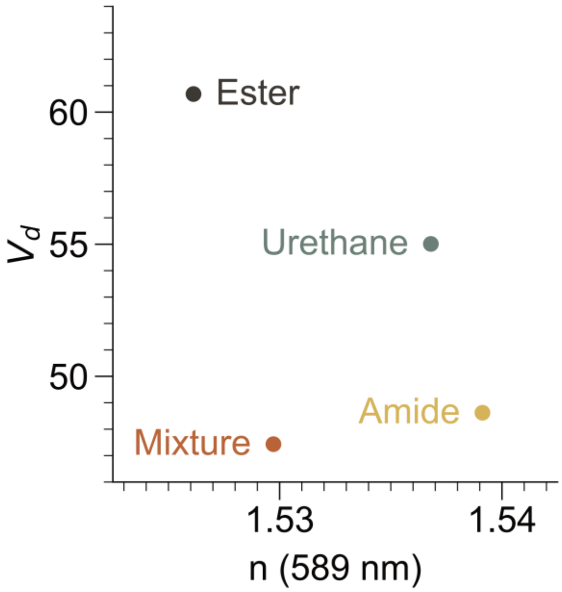

Figure S17. Abbe number (Vd) does not show any clear trend with RI or hydrogen bonding.