

Supplementary Information

Construction from destruction using a photo-triggered self-propagating degradable polyurethane as a one-pot epoxy

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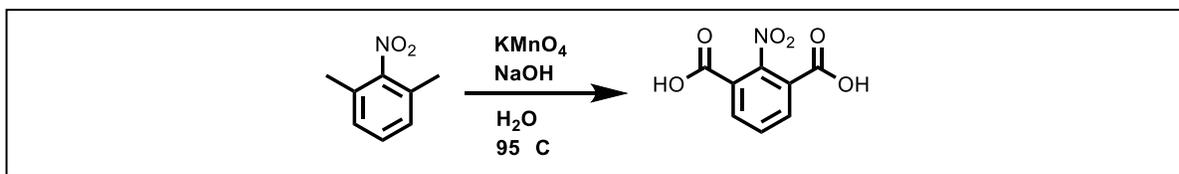
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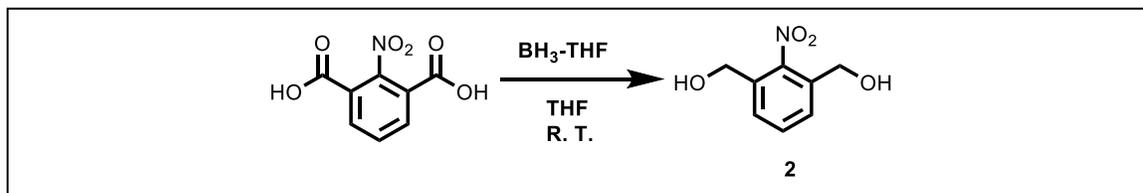
1. Materials and Instrumentation

All reagents were purchased from Acros Organics, Fisher Scientific, Chem-Impex International, AK Scientific, TCI America, or Sigma-Aldrich and used without further purification unless otherwise noted. Dried dichloromethane (DCM), pyridine, THF were obtained from an Mbraun solvent purification system. *N*-Methyl-2-pyrrolidone (NMP) was purified via vacuum distillation and stored in N₂ atmosphere with 20 wt% 3 Å molecular sieves. An UV light M365L2 (365 nm, 190 mW) from Thorlabs was used for photolysis experiments. NMR spectra were recorded using Varian U400, UI400, U500, VXR500, UI500NB, and CB500 (Bruker) spectrometers in the NMR laboratory, School of Chemical Science, University of Illinois and were processed with MestRec (v4.8.1.1) or MestReNova (v. 6.1.0). The NMR spectra were referenced to the residual proton solvent peak with coupling constants listed as Hertz (Hz). Mass spectral analyses were provided by the Mass Spectrometry Laboratory, School of Chemical Science, University of Illinois, using ESI on a Waters Micromass Q-ToF spectrometer, FD on a Waters 70-VSE spectrometer. Analytical gel permeation chromatography (GPC) experiments were performed on a hybrid system equipped with a Waters 1515 isocratic pump, a Waters 2414 refractive index detector, and a miniDAWN TREOS 3-angle laser light scattering detector (MALLS, Wyatt Technology, CA) with a detection wavelength of 658 nm. The MALLS detector was calibrated with toluene and was used to determine the absolute molecular weights. The mobile phase consisted of DMF containing 0.1 M LiBr with a flow rate of 1.0 mL/min at 50 °C using four Styragel columns (5 μm):HR 3, HR 4, and two HR 2. Absolute molecular weights of the polymers were determined based on the d_n/d_c value of each sample from the ASTRA software (version 6.1, Wyatt Technology CA) assuming 100 % mass recovery. The degradation of polymer **1** with GPC was conducted in DMF on a Tosoh Ecosec HLC8320GPC at 50 °C equipped with a reference columns (7.8 mm ID × 15 cm), guard column (6.0 mm ID × 4.0 cm × 5 μm) and two analytical columns (7.8 mm ID × 30 cm × 5 μm). The reference flowrate was set to 0.5 mL/min and the analytical column flowrate set to 1.0 mL/min. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 analyzer. About 5-10 mg of polymeric material were transferred to a platinum crucible and heated at a rate of 5 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was measured by Discovery DSC 250 from TA Instruments and T_g was calculated by half-height midpoint method on 2nd heating cycle with a heating rate 5 °C/min. Attenuated total reflection infrared spectroscopy (ATR-IR) was performed on a Nexus 670 ThermoNicolet Fourier Transform Infrared Spectrometer. Photographs were taken using an iphone 7S plus. The degradation kinetics of the crosslinked materials was quantified using Image-Pro Plus software adopting the procedure in Chapter 8: Color Segmentation in the user manual: Image-Pro Plus version 5.1 for Windows. All the data were developed and fitted using OriginPro 8.

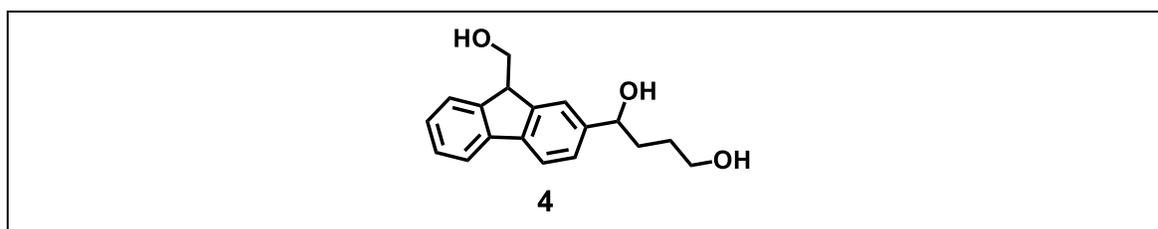
2. Monomer and Polymer Synthesis



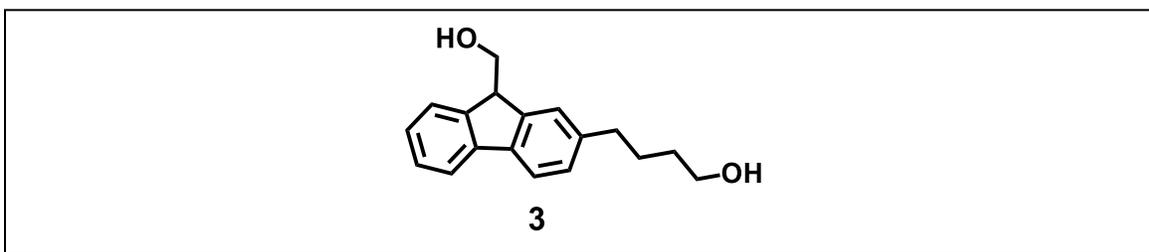
2-Nitroisophthalic acid. Synthesis and characterization of compound 2-Nitroisophthalic acid is described in S. Rajendran, R. Raghunathan, I. Hevus, R. Krishnan, A. Ugrinov, M. P. Sibi, D. C. Webster and J. Sivaguru, *Angew. Chem., Int. Ed.*, 2015, **54**, 1159-1163.



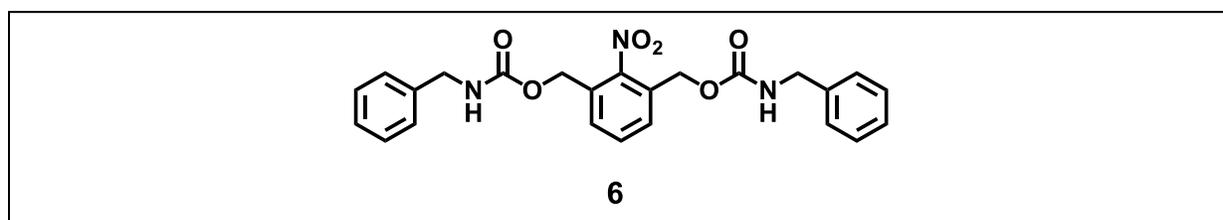
(2-Nitro-1,3-phenylene)dimethanol. Synthesis and characterization of monomer **2** is described in S. Rajendran, R. Raghunathan, I. Hevus, R. Krishnan, A. Ugrinov, M. P. Sibi, D. C. Webster and J. Sivaguru, *Angew. Chem., Int. Ed.*, 2015, **54**, 1159-1163.



1-(9-(Hydroxymethyl)-9H-fluoren-2-yl)butane-1,4-diol. Synthesis and characterization of this compound as monomer **4** is described in Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.



4-(9-Hydroxymethyl)-9H-fluoren-2-yl)butan-1-ol. Synthesis and characterization of this compound as monomer **3** is described in Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.



(2-Nitro-1,3-phenylene)bis(methylene) bis(benzylcarbamate). In a 15 mL round bottom flask, **2** (0.37 g, 2 mmol) and benzyl isocyanate (0.24 mL, 2 mmol) was dissolved in dry DCM (10 mL) and stirred for 3 min at room temperature. Dibutyltin dilaurate (126 μ L, 0.2 mmol) was added using a micro syringe. The mixture was stirred at room temperature overnight before quenching with 3 mL H₂O. The reaction was extracted with DCM (5 mL) 3 times. The combined organic layer was washed with brine (5 mL), collected, dried over MgSO₄, and concentrated under vacuum. The crude product was purified *via* silica column chromatography eluting with 5% (v/v) methanol in DCM and 270 mg (30%) of product as a colorless liquid was obtained. ¹H NMR (500 MHz, CDCl₃): δ 7.50-7.26 (*m*, 13H), 5.24 (*s*, 4H), 4.37 (*s*, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 155.8, 149.0, 138.2, 131.2, 130.1, 130.0, 128.8, 127.8, 127.6, 62.8, 45.3. High resolution ESI-MS: Calculated for C₂₄H₂₄N₃O₆⁺ ([M+H]⁺): 450.1587; obtained 450.1668.

General synthetic procedure of photo-triggered self-propagating polymer 1. In a 5 mL glass vial, **2** (9.15 mg, 0.05 mmol) and **3** (53.67 mg, 0.2 mmol) were dissolved in NMP (0.2 mL) at room temperature. Hexamethylene diisocyanate (42 μ L, 0.258 mmol) and dibutyltin dilaurate (12 μ L, 0.019 mmol) were added in sequence and the mixture was stirred at room temperature for 24 h. Benzyl alcohol (10 μ L) was added and stirred for 1 h to quench the polymerization reaction. The polymer was further purified via precipitation by dissolving the polymer in 50% (v/v) methanol in DCM (2 mL) and adding the solution dropwise in diethyl ether (8 mL). The resulting precipitate solution was subjected to centrifugation and the excess solvent was decanted, which is a process that was repeated 3 times. The purified precipitate was dried under high vacuum to afford 70 mg (67%) of product as a white solid. GPC analysis (DMF): Mn = 10 kDa; Mw = 14 kDa; PDI = 1.4.

General synthetic procedure of control linear polymer 1c. Synthesis of **1c** was performed based on previously reported procedure. Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.

General synthetic procedure of photo-triggered self-propagating polymeric network 5. In a 5 mL glass vial, monomer **2** (9.15 mg, 0.05 mmol) and monomer **4** (128 mg, 0.45 mmol) were dissolved in dry NMP (0.5 mL) at room temperature. Hexamethylene diisocyanate (88 μ L, 0.55 mmol), dibutyltin dilaurate (40 μ L, 0.064 mmol), and 0.05 mL of bromothymol blue indicator stock solution in NMP (1 mg/ 1 mL) were added in sequence and stirred at room temperature for 15 min. The solution was quickly transferred to a circular PTFE mold (2.2 cm diameter and 500 μ m thickness) and covered by a glass slide equipped with a PTFE sheet. This mixture was cured at room temperature in a vacuum oven under N_2 atmosphere for 24 h.

General synthetic procedure of photo-triggered self-propagating polymeric network 5 with encapsulation of epoxide monomer (one-pot epoxy organogel). In a 5-mL glass vial, monomer **2** (9.15 mg, 0.05 mmol) and monomer **4** (128 mg, 0.45 mmol) were dissolved in dry NMP (0.55 mL) at room temperature. Hexamethylene diisocyanate (88 μ L, 0.55 mmol) and dibutyltin dilaurate (40 μ L, 0.064 mmol) were added in sequence. Finally, 2,2-Bis(4-glycidyloxyphenyl)propane (136 mg, 0.4 mmol BADGE) was added and the solution was stirred for 15 minutes at room temperature. 0.2 mL reaction solution was quickly transferred to another 5 mL vial, reacting at room temperature under nitrogen for 24 h.

General synthetic procedure of control polymeric network 5c. Synthesis of control polymeric network **5c** with monomer **4** is described in Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.

3. GPC of polymer 1

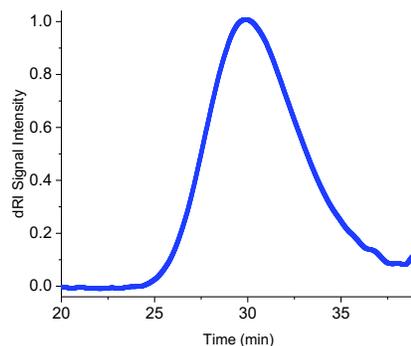


Fig. S1 Representative GPC elution curve of photo-triggered self-propagating degradable polymer **1**. $M_n = 10$ k, PDI = 1.4.

4. Supplemental DSC of Polymer 1

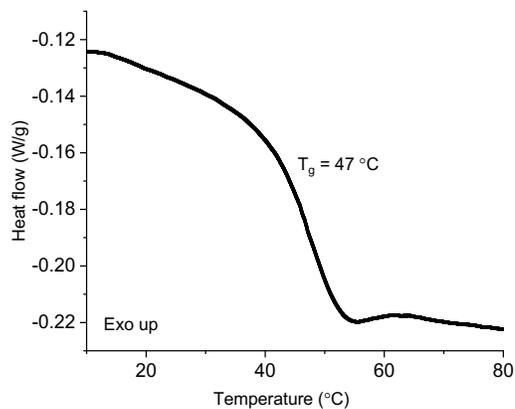


Fig. S2 DSC of photo-triggered self-propagating degradable polymer **1**. “Exo up” indicates that the direction of exothermic heat flow is up. T_g was calculated by half-height midpoint method on 2nd heating cycle with a heating rate is 5 °C/min.

5. Supplemental TGA of Polymer 1

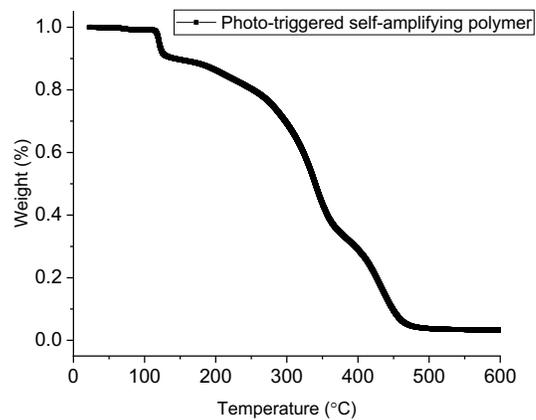


Fig. S3 TGA data of photo-triggered self-propagating degradable polymer **1** with ramping temperature at the rate of 5°C/min. The temperature for 5% weight loss is 120 °C.

6. ESI-MS of degraded products of 6

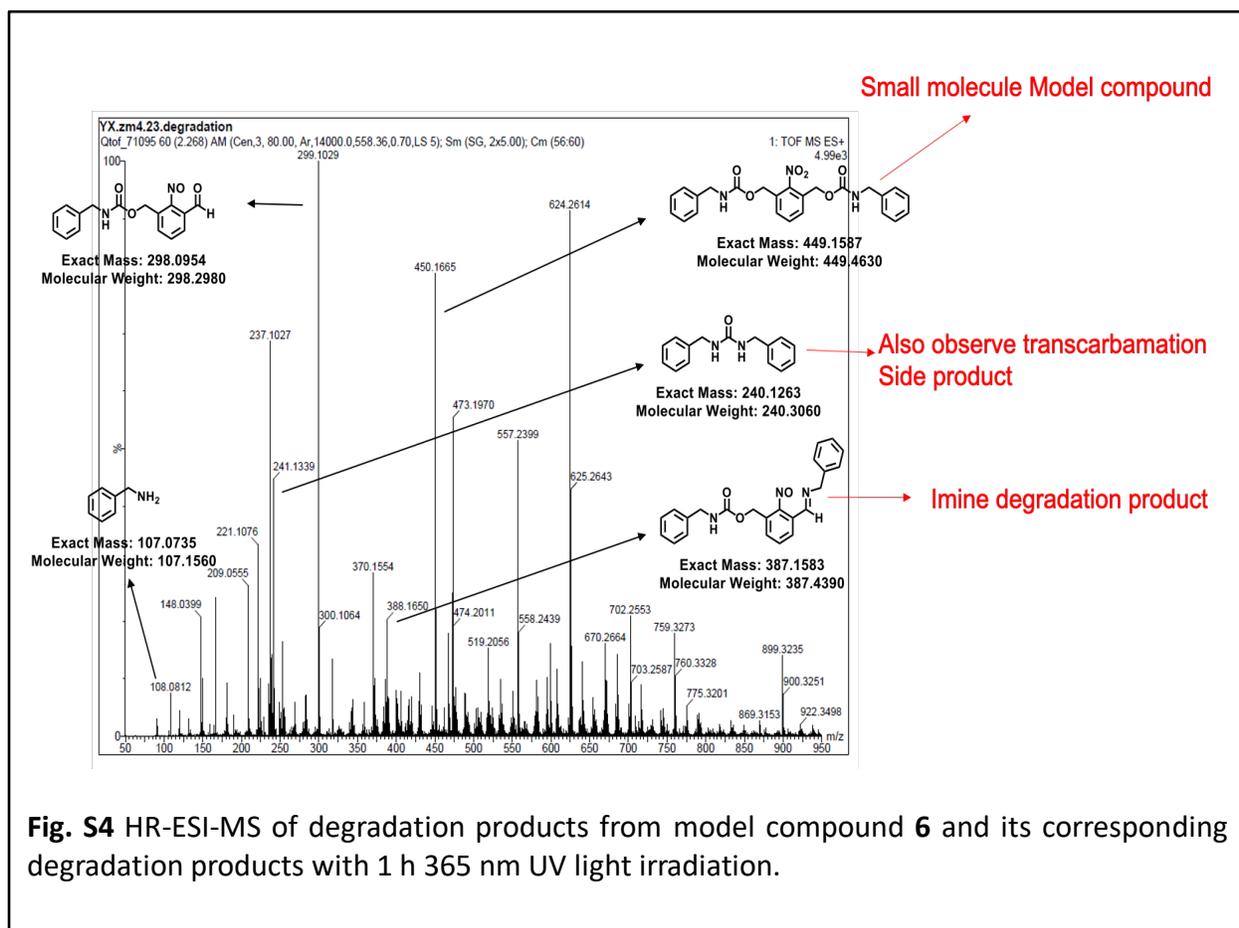
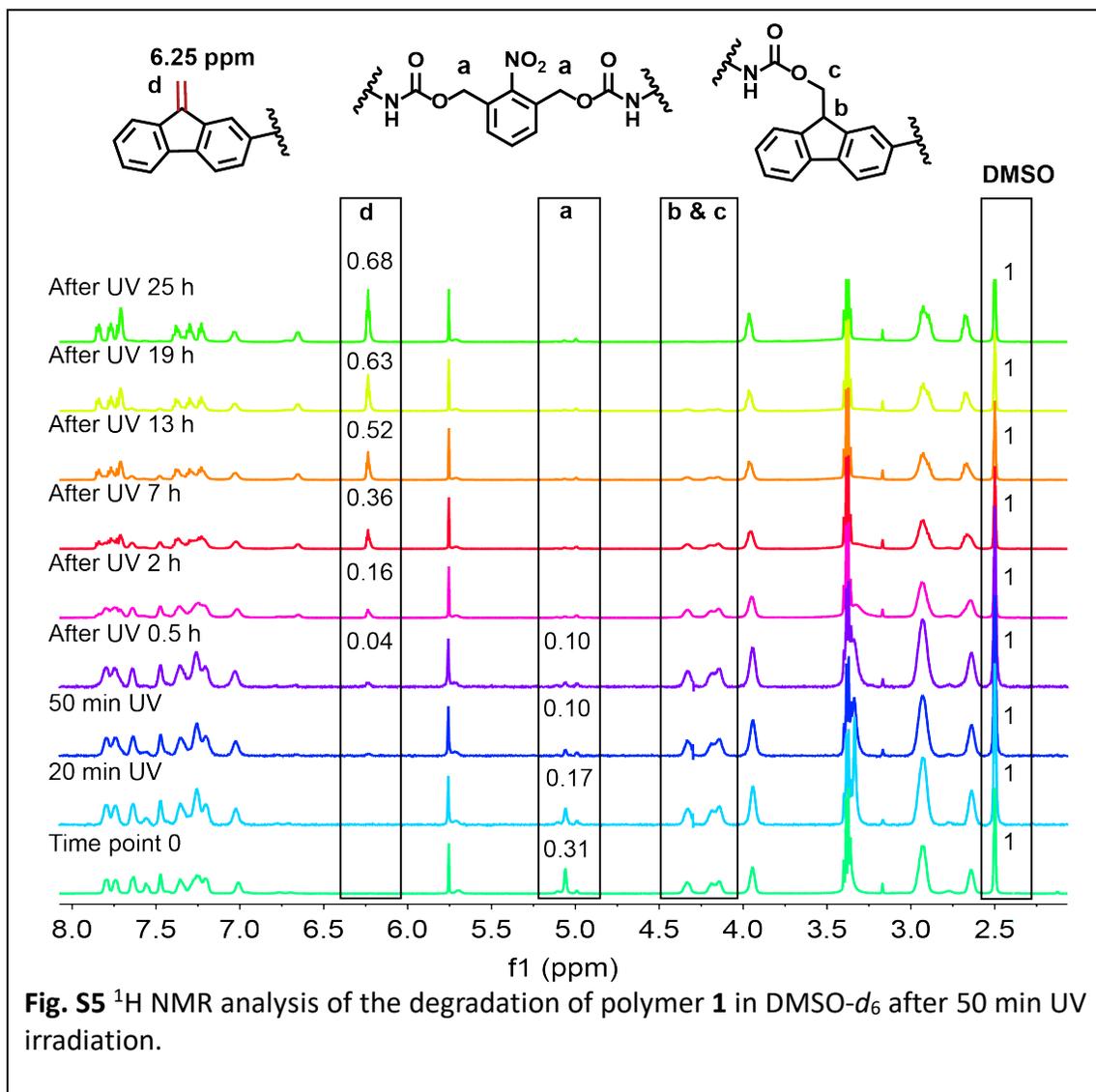


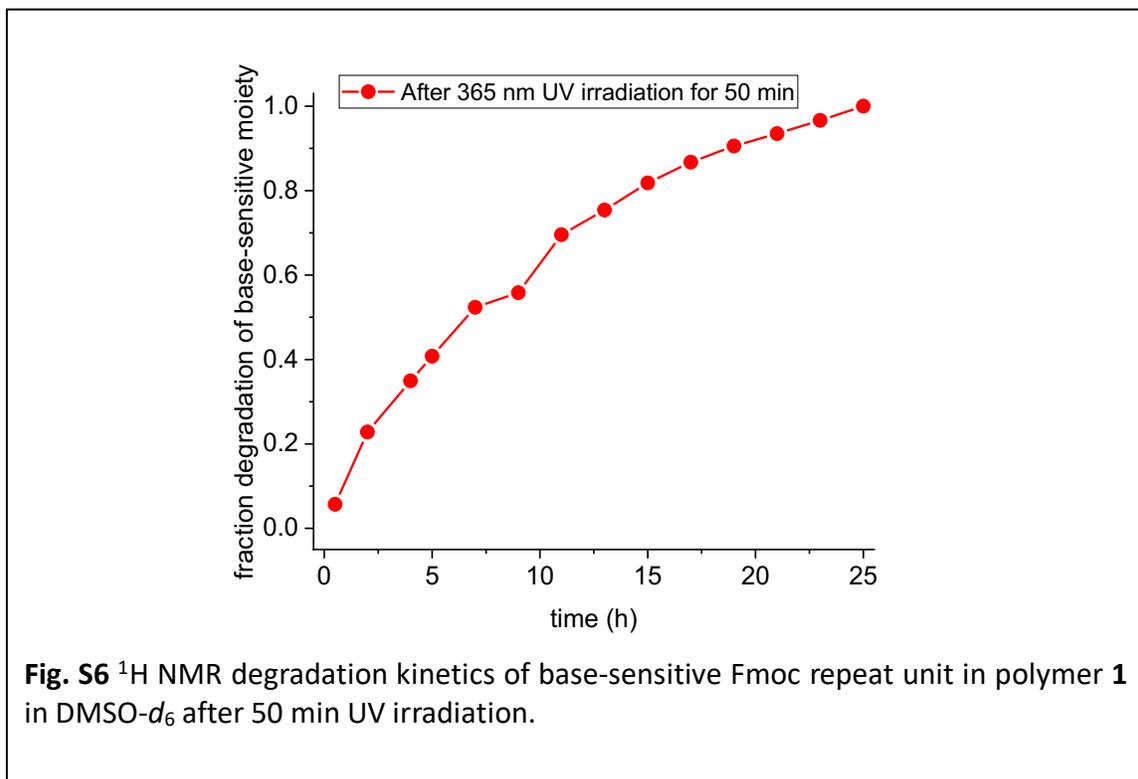
Fig. S4 HR-ESI-MS of degradation products from model compound **6** and its corresponding degradation products with 1 h 365 nm UV light irradiation.

7. NMR and GPC Degradation Study of Linear Polymer 1

General procedure for the ^1H NMR analysis of photo-triggered degradation of polymers.

A 5 mL vial was charged with about 5.4 mg of polymer and 0.5 mL (11 mg/mL) $\text{DMSO}-d_6$. This mixture was sonicated for 5 min and transferred to an NMR tube using a 1 mL syringe. An ^1H NMR of the polymer sample was performed before UV exposure, and after 20 and 50 min UV irradiation. The degradation kinetics of the polymer was monitored by obtaining the relative ratios between the Fmoc unit elimination product with proton signal at δ 6.25 ppm with respect to the $\text{DMSO}-d_6$ peak at different time points over 25 h.





General procedure for the photo-triggered degradation of linear polymer **1** by GPC.

A 10 mg/ mL solution of polymer **1** in DMF with 0.1 M LiBr was prepared and was filtered through a 0.45 μm syringe filter. The polymer solution was irradiated for 50 min by 365 nm UV light before taking 50 μL aliquots at various time points for GPC analysis.

8. NMR Degradation Study of Linear Polymer **1** With Base Addition

General procedure for ¹H NMR analysis of base-triggered degradation of polymer **1**.

A 5 mL vial was charged with about 5 mg of polymer **1** and 0.5 mL DMSO-*d*₆. This mixture was sonicated for 5 min and transferred to an NMR tube using a 1 mL syringe. An ¹H NMR of the polymer degradation was performed after addition of 5% hexylamine corresponding to Fmoc repeating unit concentration. The degradation kinetics of the polymer was monitored by obtaining the relative ratios between the Fmoc unit elimination product at δ 6.25 ppm with respect to the DMSO-*d*₆ peak at different time points. The degradation percentage versus time data was used to fit a sigmoidal degradation equation and *k*₁ as well as *k*₂ value was calculated.²

$$\frac{c}{c_0} = \frac{k_1 + k_2 c_0}{k_1 e^{(k_1 + k_2 c_0)t} + k_2 c_0} \quad (\text{S1})$$

Where *c* is the concentration of the base-triggered degradable Fmoc repeat unit with its initial

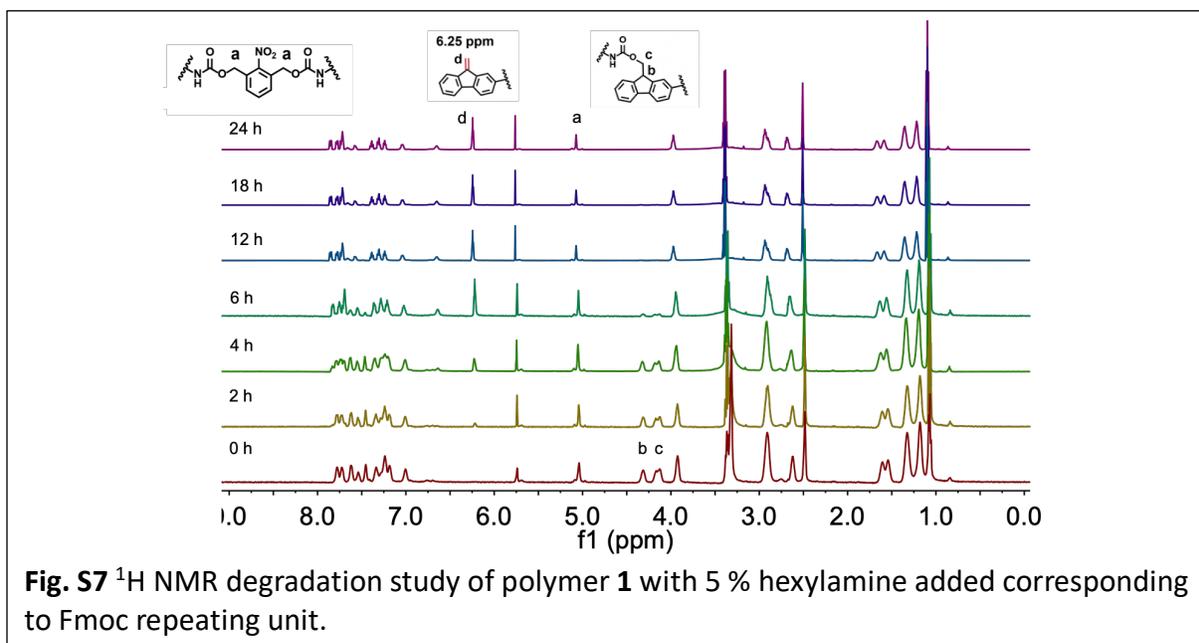
concentration value being c_0 . The c_0 values used were 0.019 M. After fitting the degradation data with addition of 5% hexylamine as base into equation S1,

$$k_1 = 3.4 \times 10^{-3} \text{ min}^{-1}$$

$$k_2 = 0.20 \text{ M}^{-1} \text{ min}^{-1},$$

$$k_2 c_0 = 3.8 \times 10^{-3} \text{ min}^{-1}$$

$$k_2 c_0 > k_1, \frac{k_2 c_0}{k_1} = 1.12$$



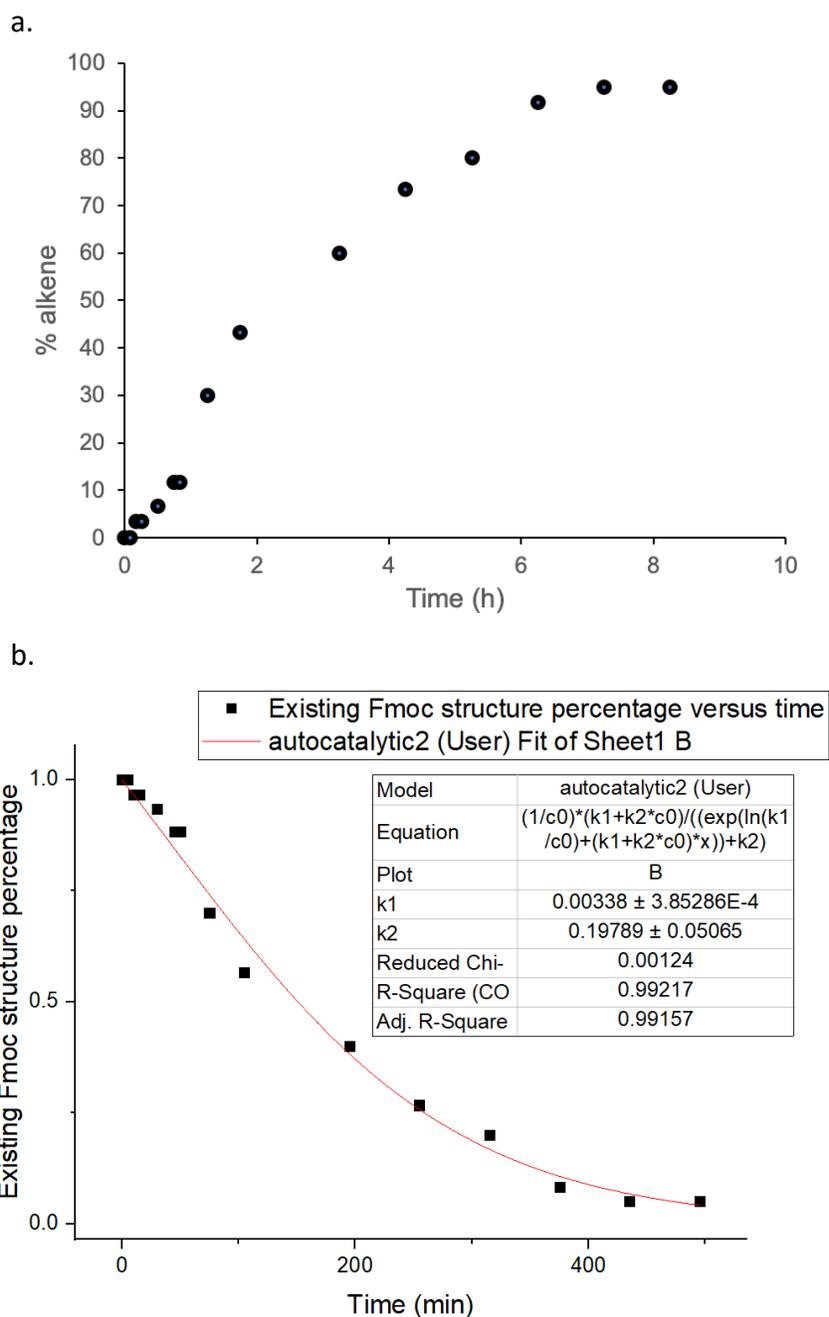


Fig. S8 (a) Degradation percentage of polymer **1** versus time with addition of 5 % hexylamine corresponding to Fmoc repeat unit. The percent conversion of Fmoc moiety to alkene were determined by the absolute ratio between the alkene peak (δ 6.25 ppm) and DMSO- d_6 over time. (b) Representative data fitting of degradation of Fmoc repeat unit with addition of 5 % hexylamine as trigger. The Fmoc repeat unit concentration is 19 mM solution in DMSO- d_6 at 25 °C. The red line represents the fitting curve of the data to equation S1 ($R^2 = 0.992$).

9. ESI-MS Analysis of the Degradation Products from Polymer 1

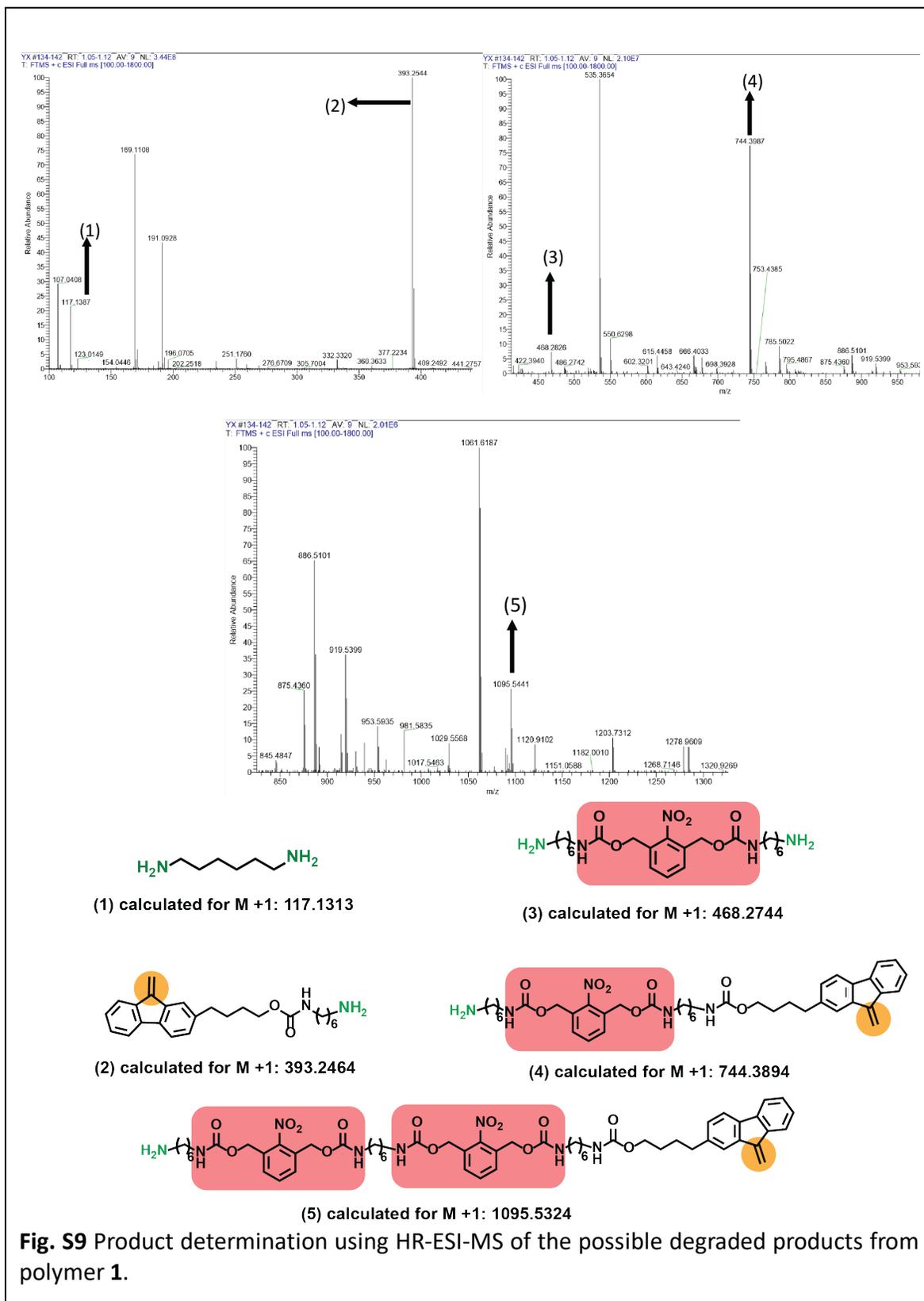
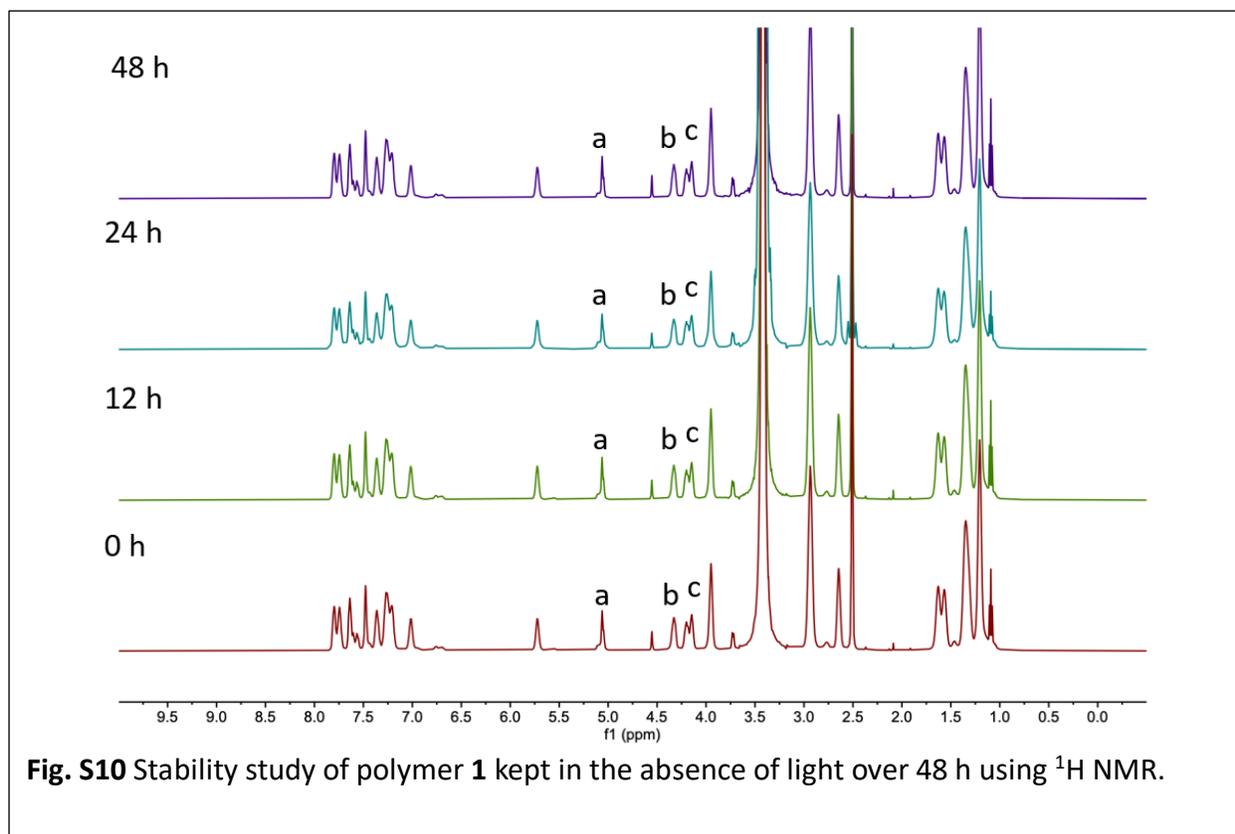


Fig. S9 Product determination using HR-ESI-MS of the possible degraded products from polymer 1.

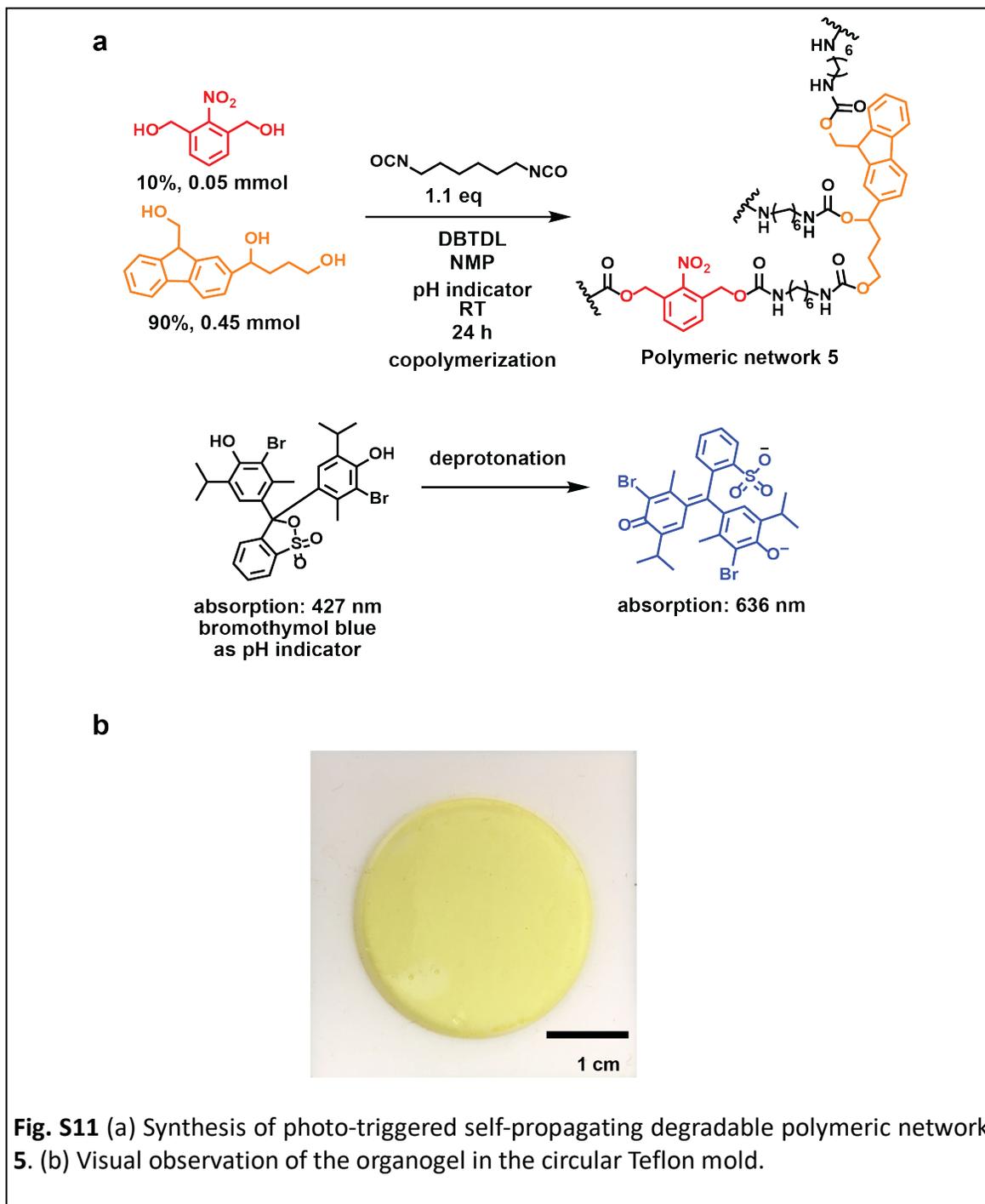
10. Stability Study of Polymer 1 by ^1H NMR

General procedure for the ^1H NMR analysis of stability of polymer 1.

A 5 mL vial was charged with about 5 mg of polymer 1 and 0.5 mL $\text{DMSO-}d_6$. The mixture was sonicated for 5 min and transferred to an NMR tube using a 1 mL syringe. The sample was kept in the dark and ^1H NMR of the polymer sample was performed at different time points over 48 h.



11. Synthesis and Characterization of Polymeric Network 5



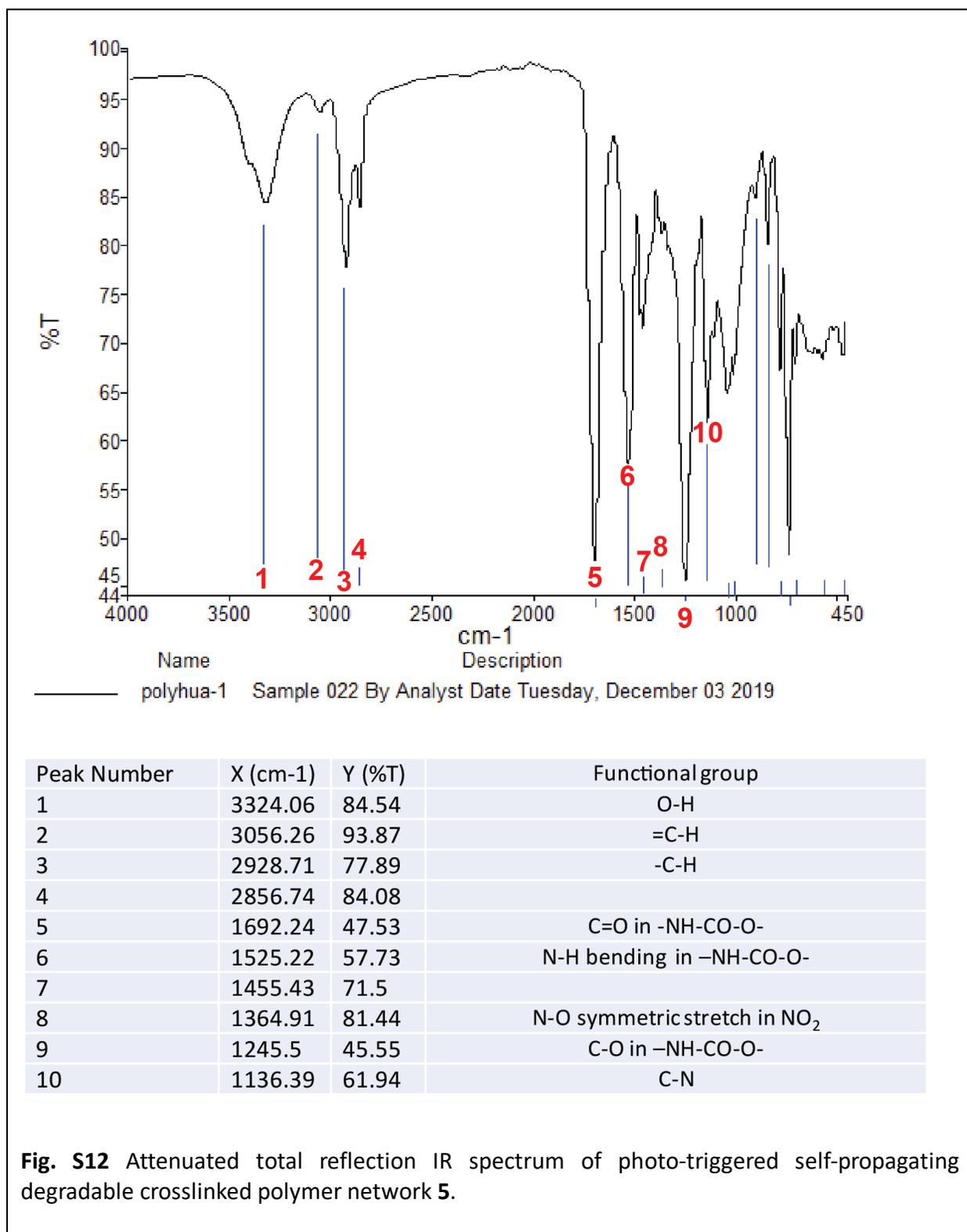
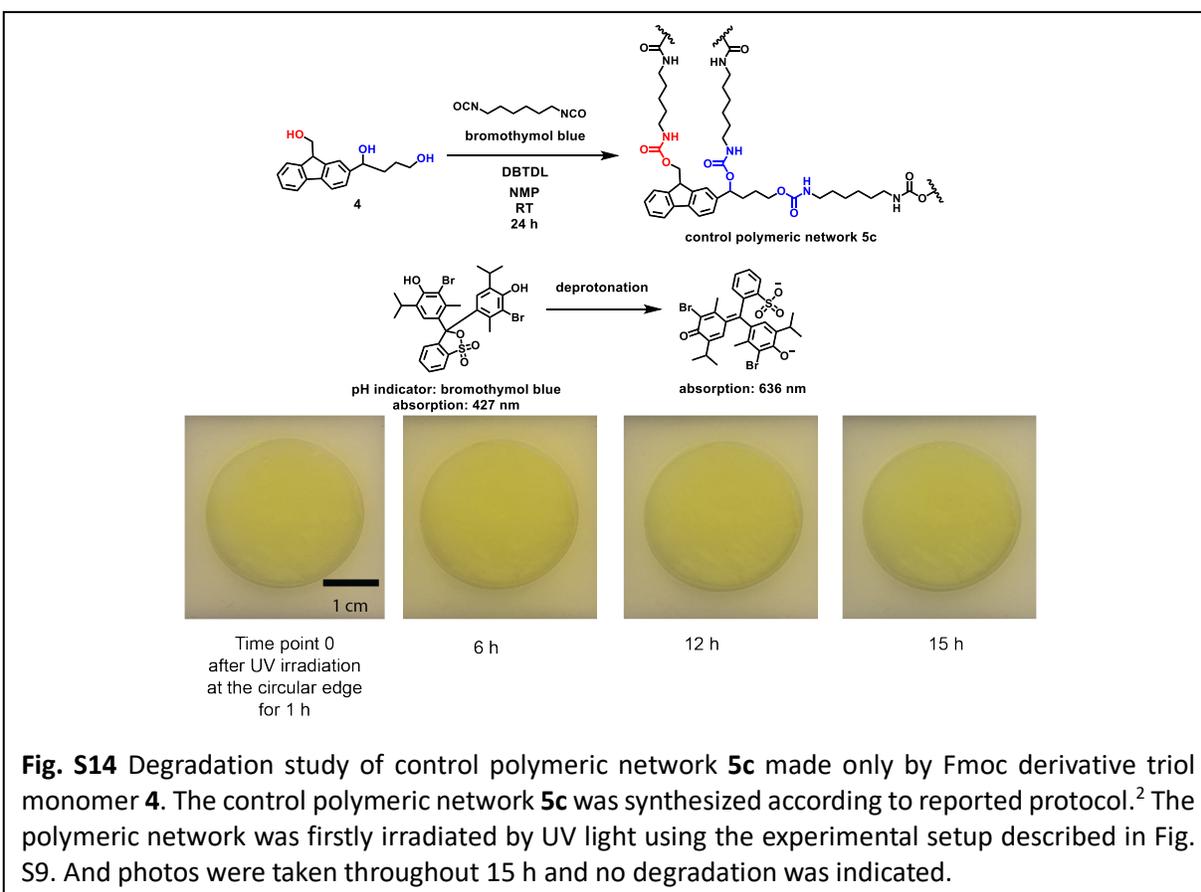
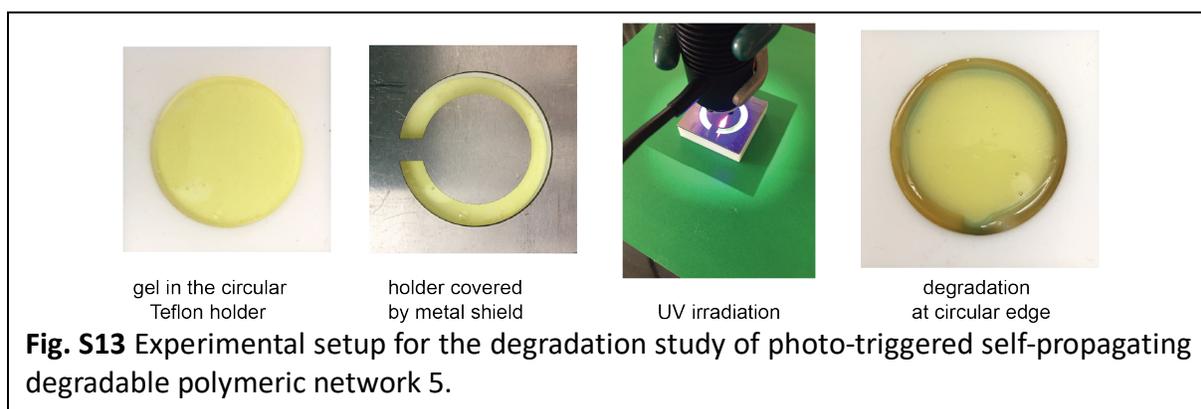


Fig. S12 Attenuated total reflection IR spectrum of photo-triggered self-propagating degradable crosslinked polymer network 5.

12. Degradation Study of Degradable Polymeric Network 5.

A dye solution was prepared by dissolving 1 mg of bromothymol blue in 1 mL NMP. About 5 mL of dye solution was used to swell the gel for 3 h. A circular aluminum cutout was pressed against the gel to obtain a circular gel with a 29 mm diameter. The gel was then placed onto a 29 mm diameter Teflon mold and covered with an aluminum shield that only exposed the edge of the gel. The gel was irradiated by UV light for 1 h and allowed to degrade and photos were taken every 10 min. The fraction of color change (the area with color change to green blue) of the gel was quantified and plotted against time using an Image-Pro-Plus software. Quantification of degradation area percentage through Image-Pro-Plus was conducted using reported procedure.²



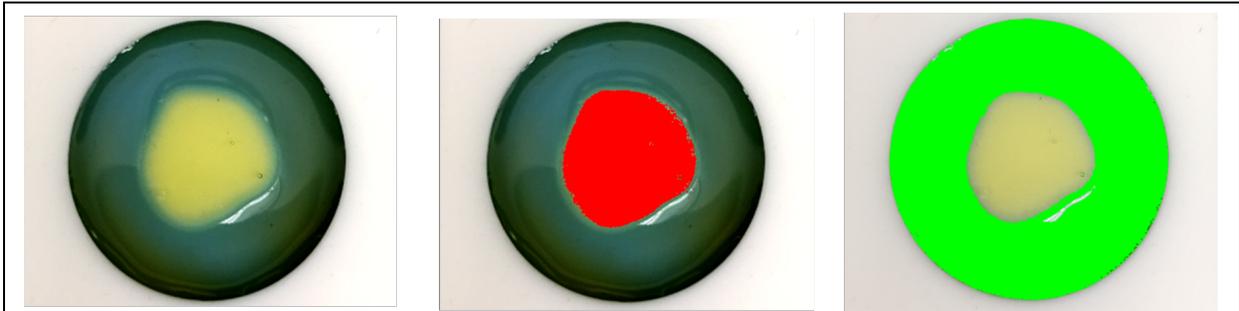


Fig. S15 Example of performing non-degraded yellow area color and degraded non-yellow area color segmentation in Image-Pro-Plus.

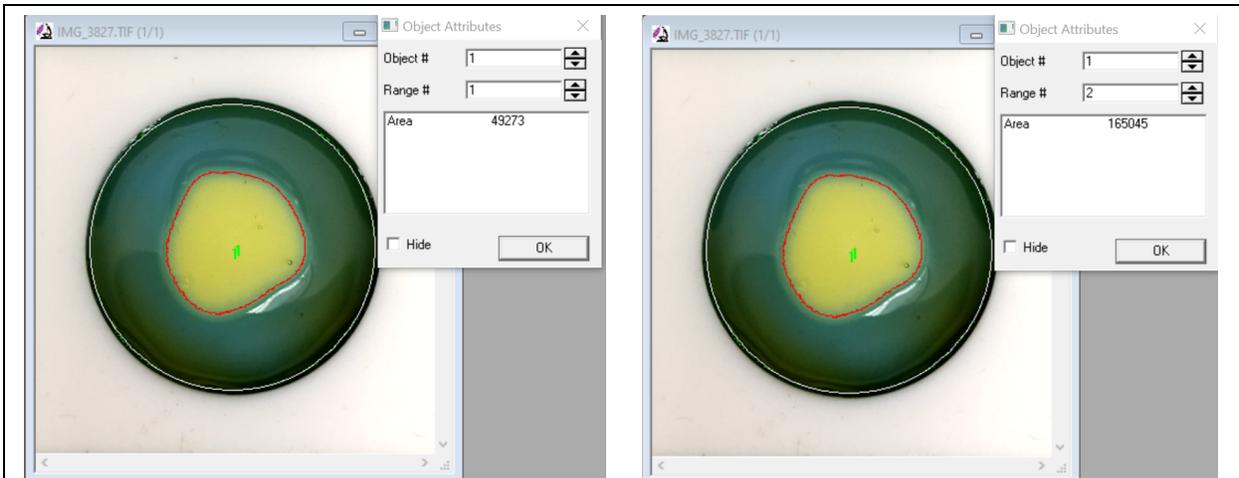


Fig. S16 Example of counting the area of non-degraded yellow area(left) and degraded non-yellow area(right) in Image-Pro-Plus.

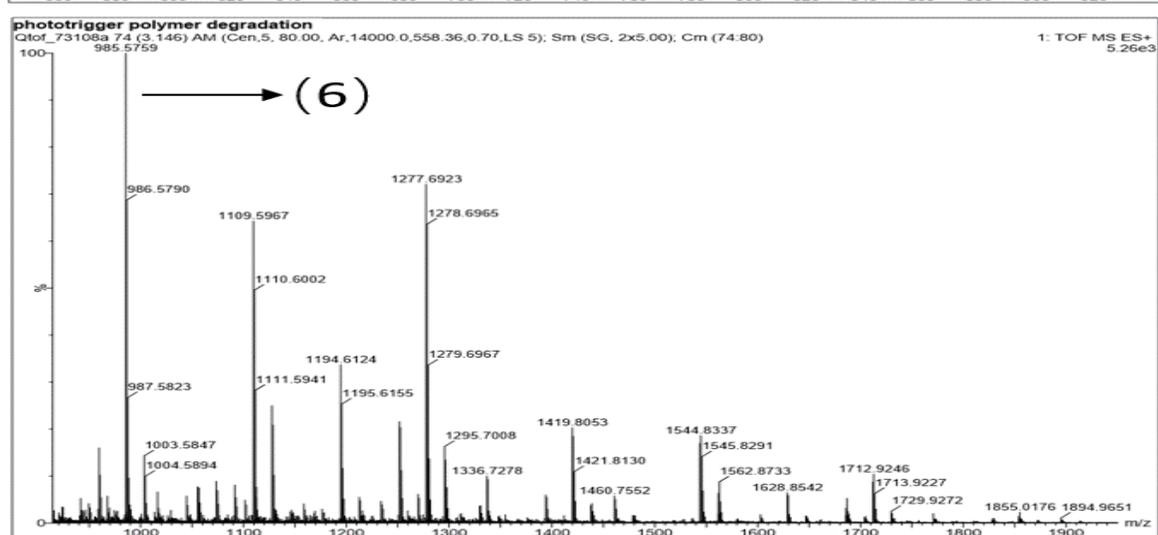
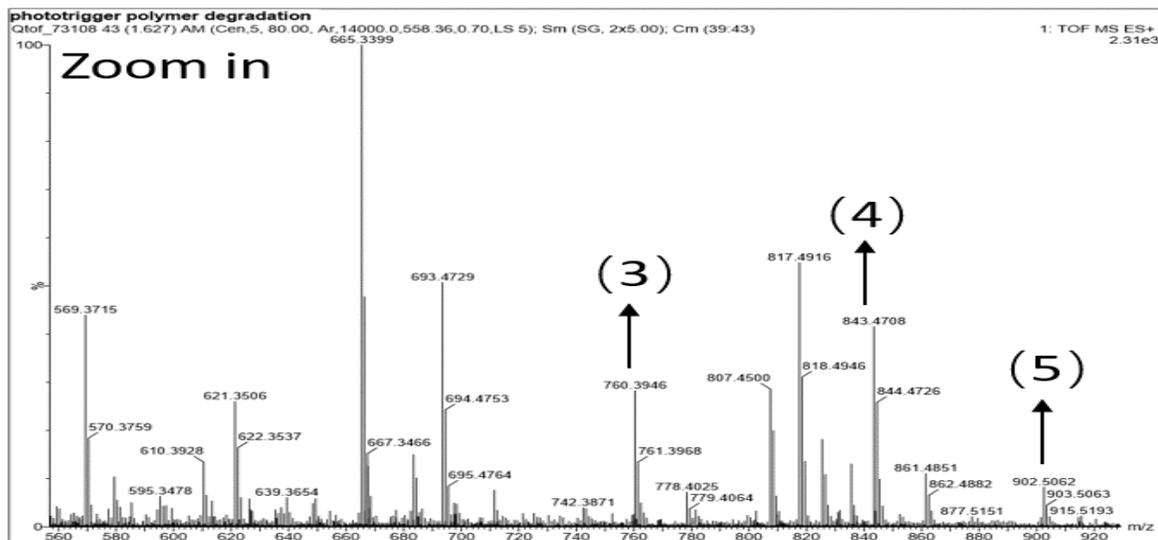
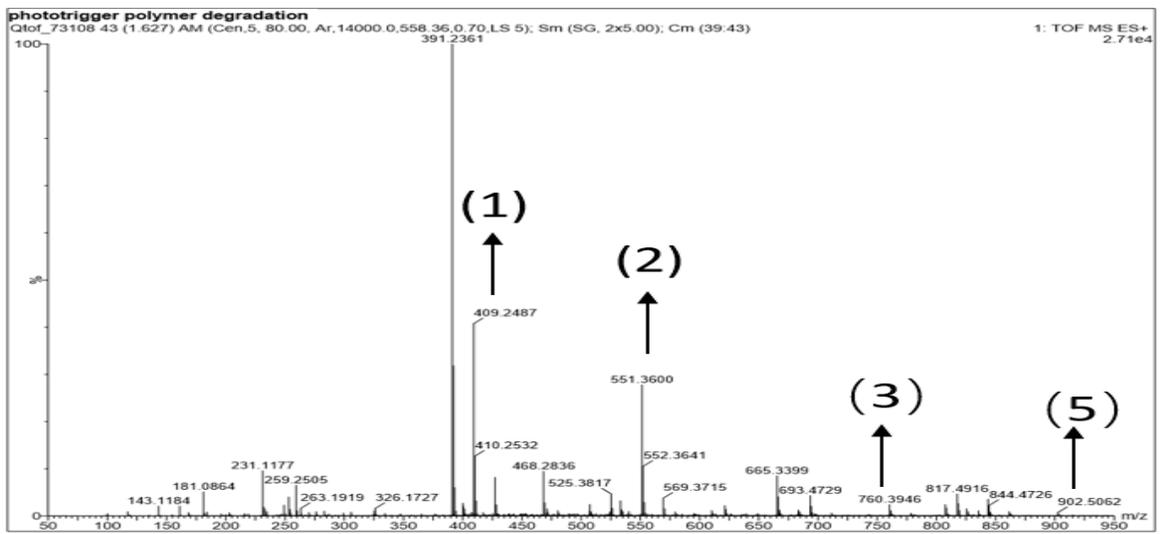
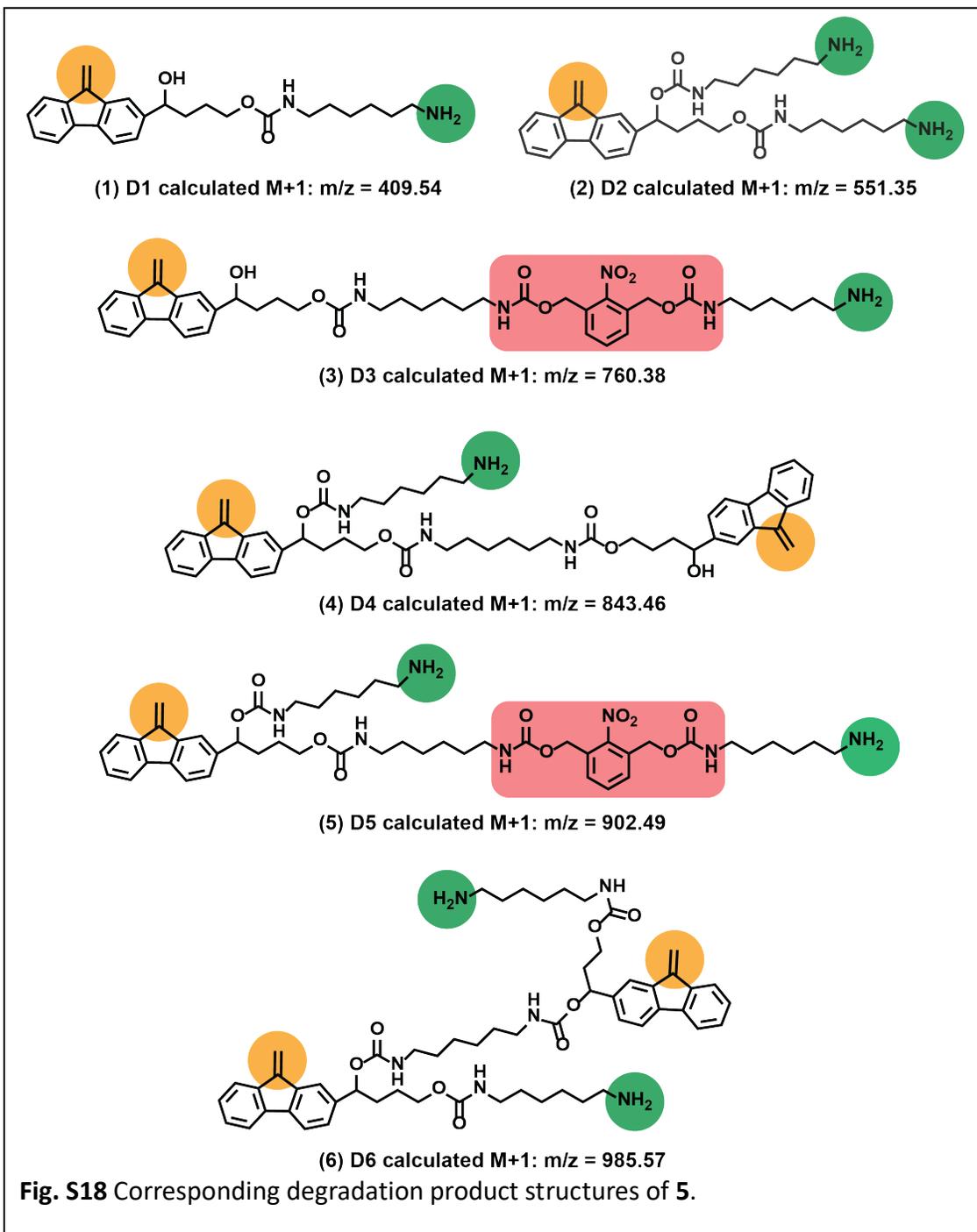


Fig. S17 HR-ESI-MS of degradation product from 5.



13. Degradation of one-pot epoxy polyurethane organogel and synthesis of adhesive

The crosslinked gel 5 with BADGE epoxide monomer encapsulation beforehand (one-pot epoxy polyurethane organogel) was swelled in 0.2 mL of NMP and was irradiated by 365 nm UV light for 2 h. After irradiation, the gel swollen was allowed to degrade at room temperature. After 9 h the gel transitioned into a liquid and was concentrated by removing excess NMP by purging with N₂ until about 1 M concentration of degraded amine solution. About 10 mg of degradation mixture were applied to stick together two glass slides with 1 inch × 0.5 inch overlap. The glass slides were held together with binder clips and cured in an oven at 95 °C.

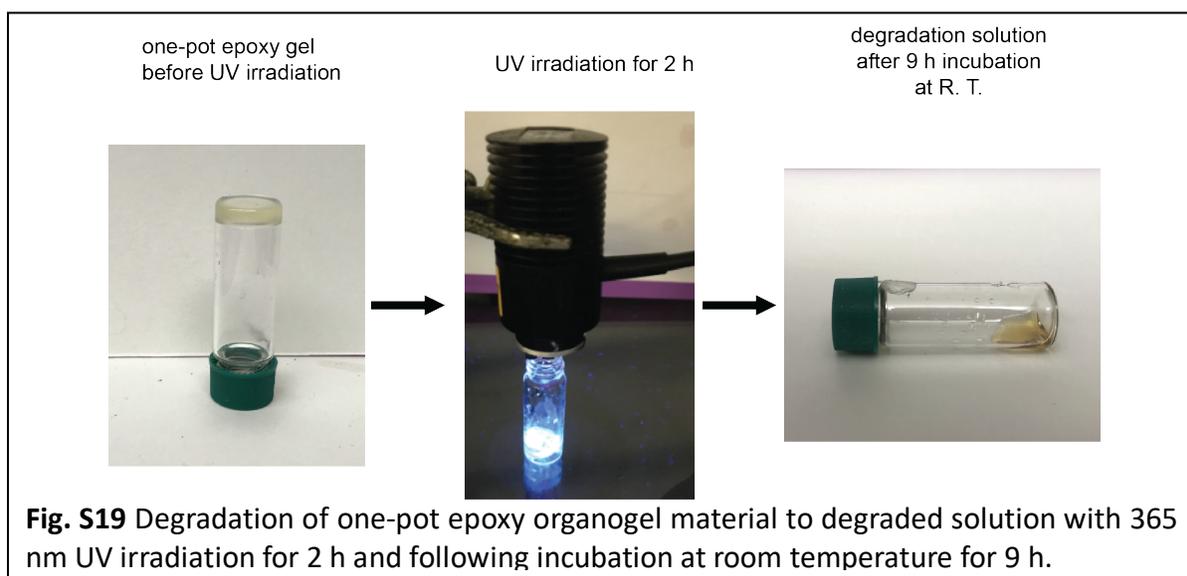


Fig. S19 Degradation of one-pot epoxy organogel material to degraded solution with 365 nm UV irradiation for 2 h and following incubation at room temperature for 9 h.

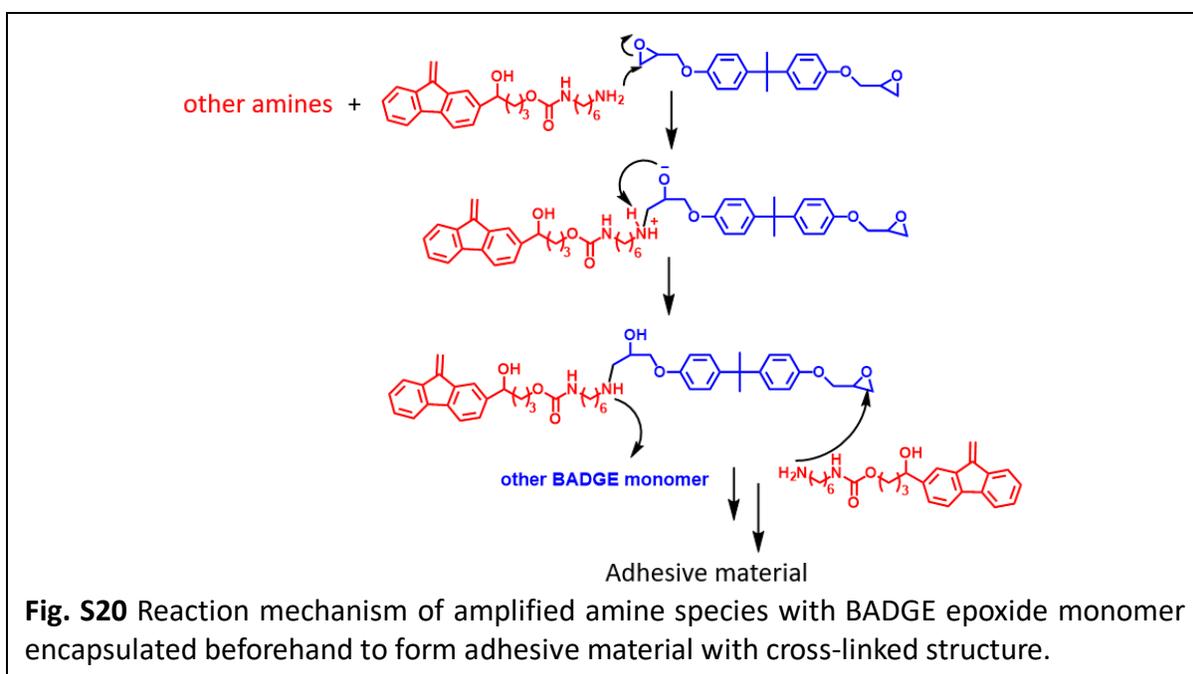
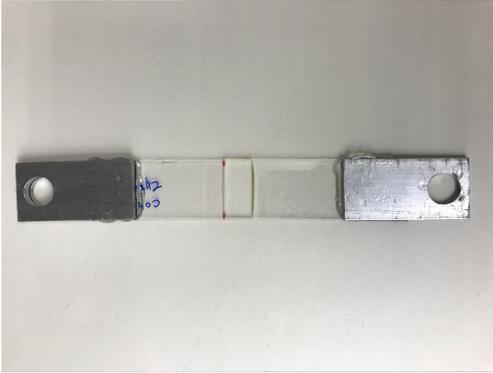


Fig. S20 Reaction mechanism of amplified amine species with BADGE epoxide monomer encapsulated beforehand to form adhesive material with cross-linked structure.

a

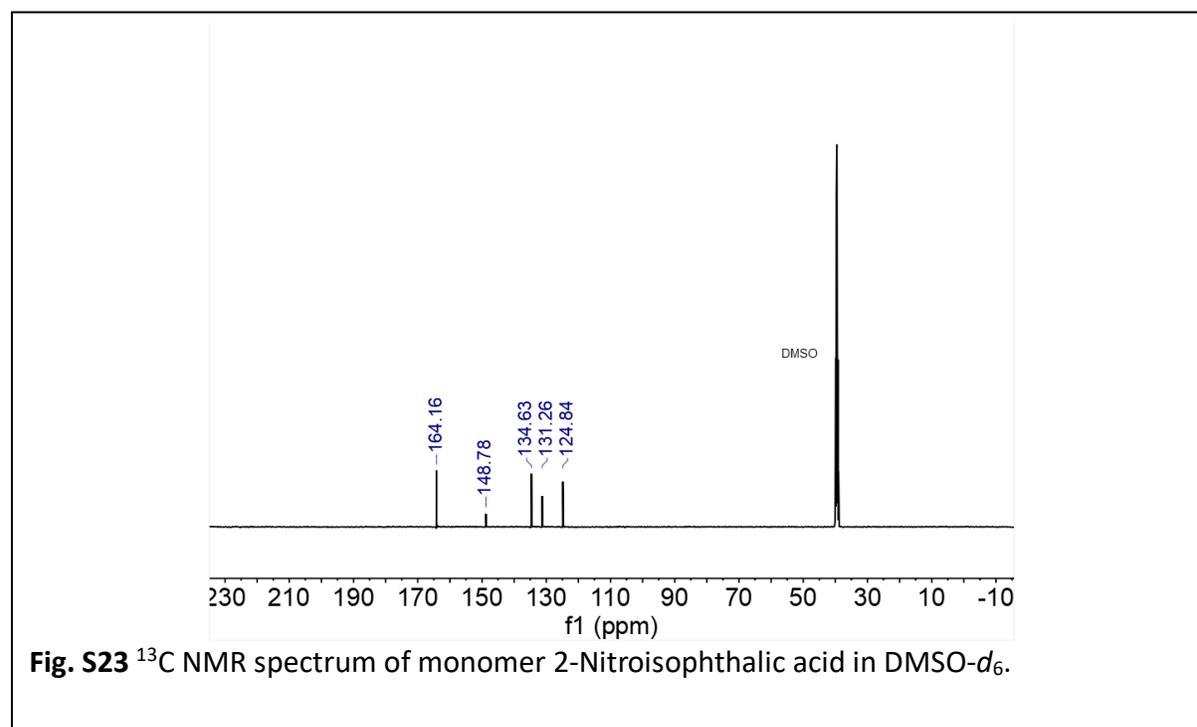
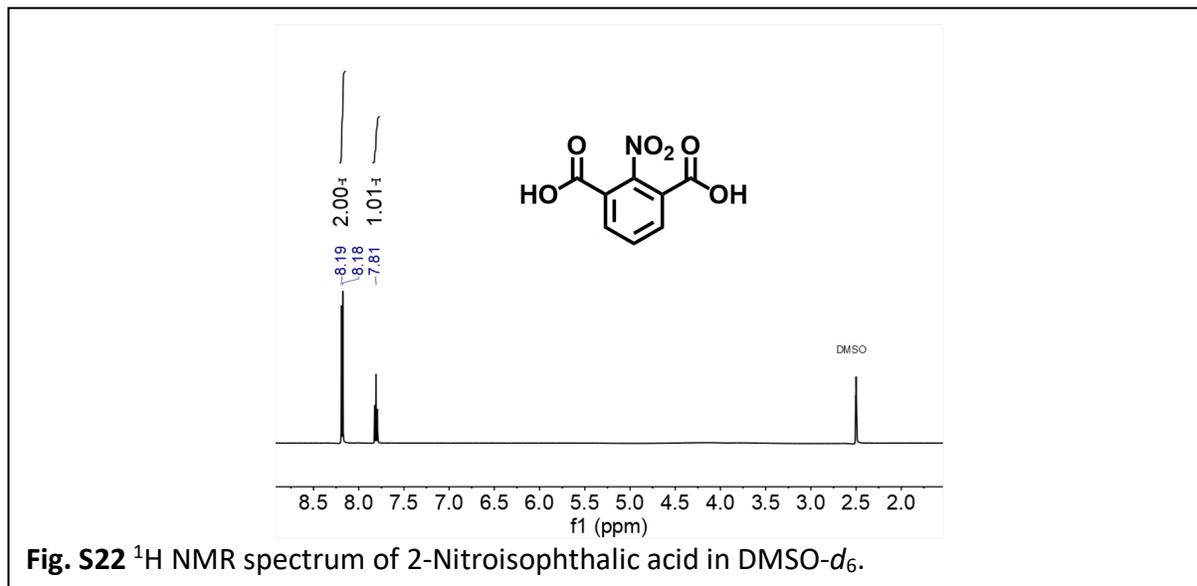


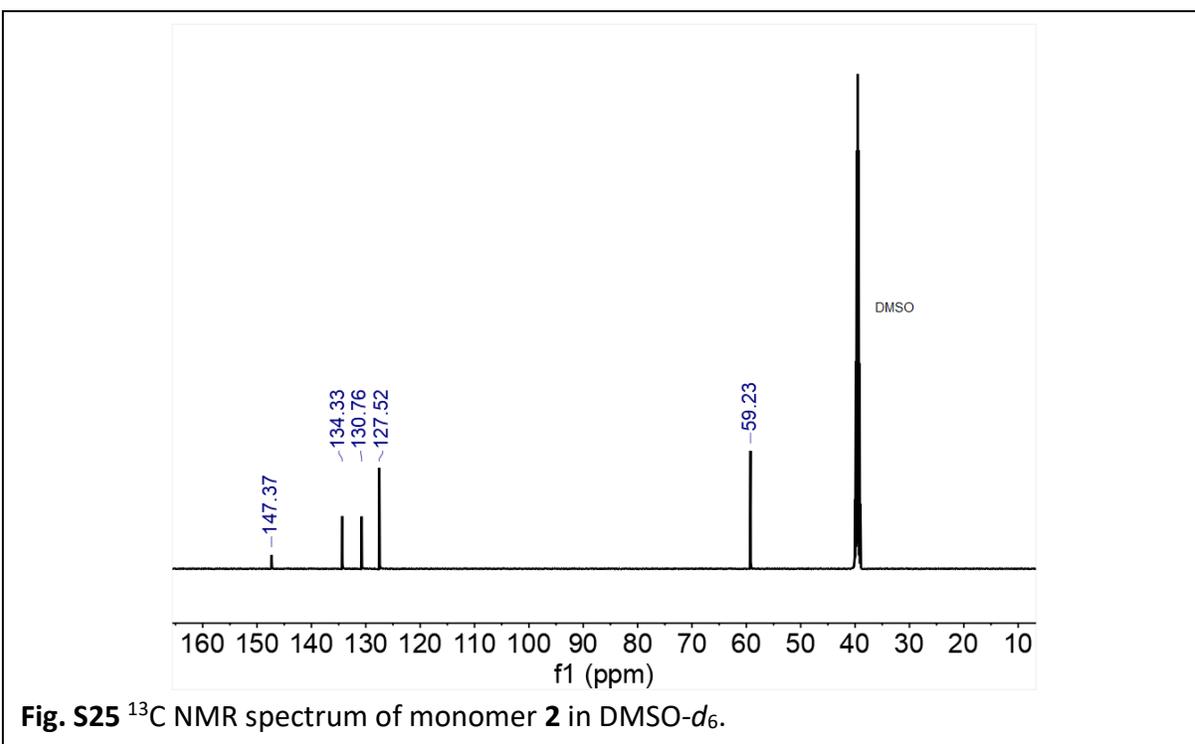
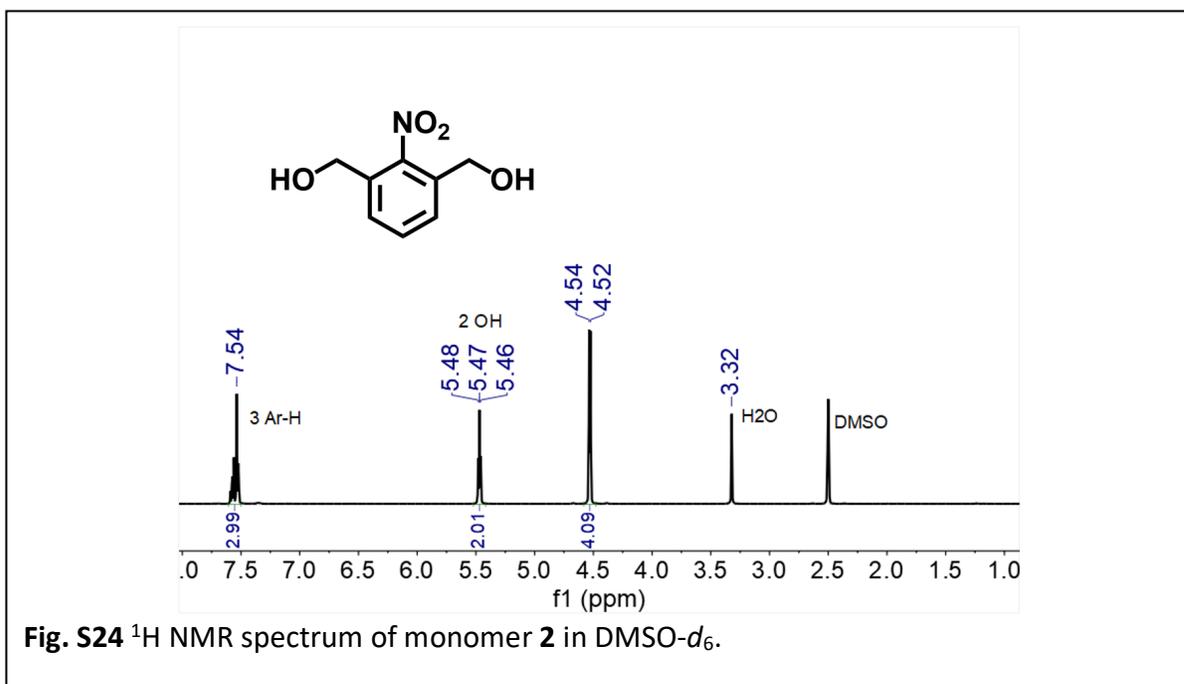
b

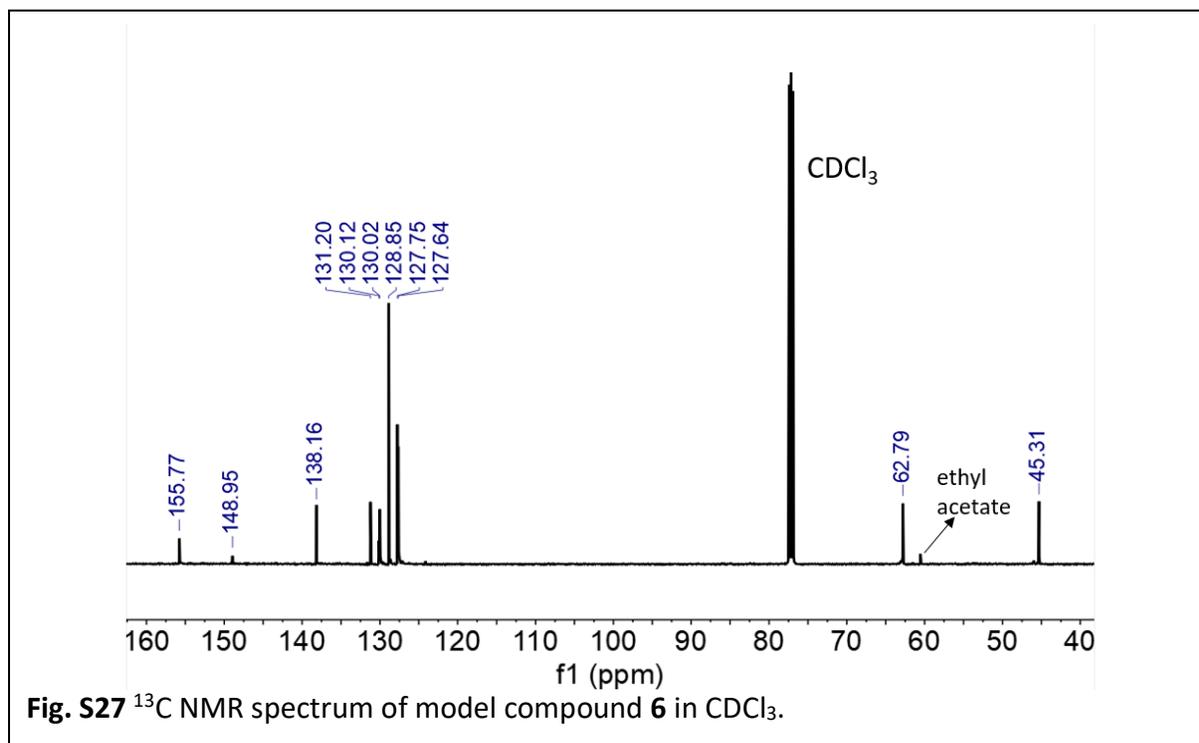
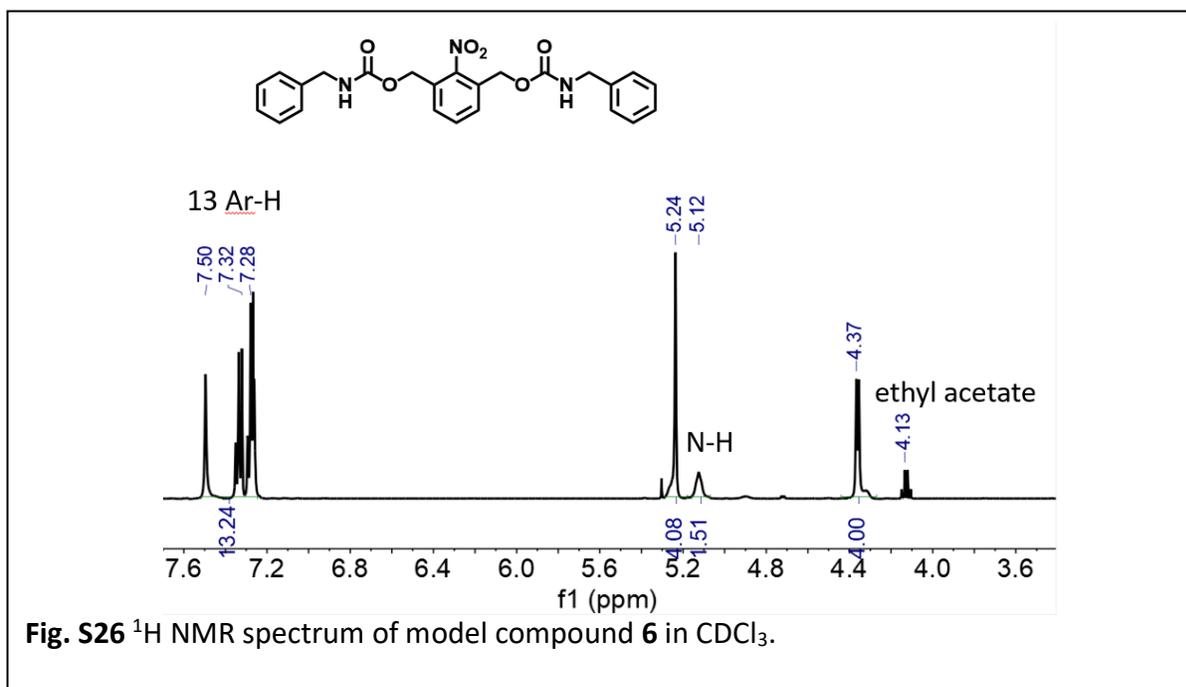


Fig. S21 (a) Left: the adhesive sample prepared for lap shear test. Right: the microscope glass substrate got broken after shear strength reached 2.2 Mpa. (b) Left: adhesive sample is enough to hold 20 pound kettlebell. Right: zoom in photo of 20 pound kettle bell.

14. Monomer Characterization







15. References

1. S. Rajendran, R. Raghunathan, I. Hevus, R. Krishnan, A. Ugrinov, M. P. Sibi, D. C. Webster and J. Sivaguru, *Angew. Chem., Int. Ed.*, 2015, **54**, 1159-1163.
2. Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.