

Supporting Information (SI)

# Folding Fluorescent Probes for Self-Reporting Transesterification in Dynamic Polymer Networks

*Sheng Wang,<sup>1</sup> Hong Wang,<sup>2</sup> Peisheng Zhang,<sup>2</sup> Lulu Xue,<sup>1</sup> Jian Chen,<sup>2\*</sup> and Jiaxi Cui<sup>1,3\*</sup>*

1. INM – Leibniz Institute for New Materials Campus D2 2, Saarbrücken 66123, Germany.
2. Key Laboratory of Theoretical Organic Chemistry and Functional Molecule of Ministry of Education, Hunan Provincial Key Laboratory of Controllable Preparation and Functional Application of Fine Polymers, Hunan Province College Key Laboratory of QSAR/QSPR School of Chemistry and Chemical Engineering, Hunan Provincial Key Lab of Advanced Materials for New Energy Storage and Conversion, Hunan University of Science and Technology, Xiangtan, Hunan 411201, China.
3. Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, Sichuan 610054, China

\*Corresponding Author: [Jiaxi.Cui@uestc.edu.cn](mailto:Jiaxi.Cui@uestc.edu.cn) (J. Cui); [cj0066@gmail.com](mailto:cj0066@gmail.com) (J. Chen)

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## 1. Materials and methods

### Materials

4-Hydroxybutyl acrylate (97%, TCI) was passed through a column of basic alumina. Chloroform-d ( $\text{CDCl}_3$ , 99.96 atom% D, contains 0.03% (v/v) TMS, Sigma-Aldrich), chloroform ( $\text{CHCl}_3$ , 99%, Sigma-Aldrich), methanol ( $\text{CH}_3\text{OH}$ , 99%, Alfa Aesar), benzenesulfonic acid (BSA, 98%, Sigma-Aldrich), pentaerythritol tetrakis(3-mercaptopropionate) (PTMP, 95%, Sigma-Aldrich), glycerol dimethacrylate (GDMA, Sigma-Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, Sigma-Aldrich), poly(ethylene glycol) diacrylate (PEGDA,  $M_n \sim 700$ , Sigma-Aldrich), triphenylsulfonium triflate (TPST, Sigma-Aldrich), dibutyltin dilaurate (DBTDL, 95%, Alfa Aesar) were used as received. PDI-dimer was prepared according to the procedure in our previous report.

### Methods

$^1\text{H}$  NMR spectra were performed on a Bruker ARX 300 instrument using  $\text{CDCl}_3$  as the solvent and tetramethylsilane as the internal standard. UV-vis absorption measurements were recorded on a Varian Cary 1E UV-vis spectrometer. Fluorescence spectra were carried out on an F-7000 fluorescence spectrophotometer with a R928F-PMT. Electrospray ionization mass spectrometry (ESI-MS) were recorded with QTos Ultima 3.

Tensile and compression tests were measured at room temperature using an Instron 3365 instrument with a 2 kN load cell and a deformation rate of 10 mm/min. Cylindrical shape samples (4 mm thickness  $\times$  10 mm diameter) and dog-bone shape samples (5 mm  $\times$  2 mm  $\times$  20 mm gauge length) were used for compression and tensile tests, respectively.

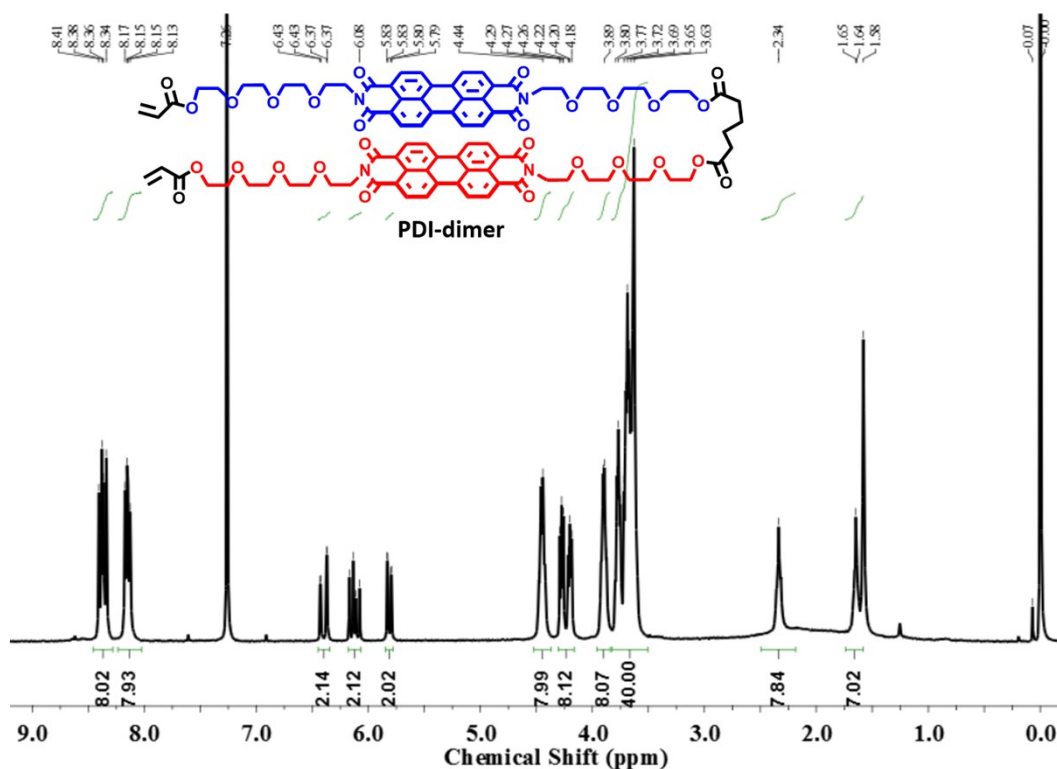
DMA tester (Q800 DMA, TA Instruments) was used to characterize the thermomechanical properties in the tensile film mode. Samples with the dimension of 15 mm  $\times$  5 mm  $\times$  1 mm were tested at a frequency of 1 Hz and an amplitude of 30  $\mu\text{m}$ . The temperature was first equilibrated at -90  $^\circ\text{C}$  for 10 min, and then increased at a heating rate of 3  $^\circ\text{C}/\text{min}$ . The glass transition temperatures ( $T_g$ ) were determined from the peak of the  $\tan\delta$ .

Stress relaxation tests were performed on the DMA tester (Q800 DMA, TA Instruments) using tensile film mode on rectangular samples (15 mm  $\times$  5 mm  $\times$  1 mm). After loading, the sample was equilibrated at the specified temperature (from 100 to 150  $^\circ\text{C}$ ) for 6 min. A constant deflection of 0.15 mm was applied to monitor the stress relaxation for different times.

For spatial transesterification, the hardness and modulus of elasticity were measured by instrumented indenter (FISCHERSCOPE HM2000) using a spherical-conical diamond indenter.

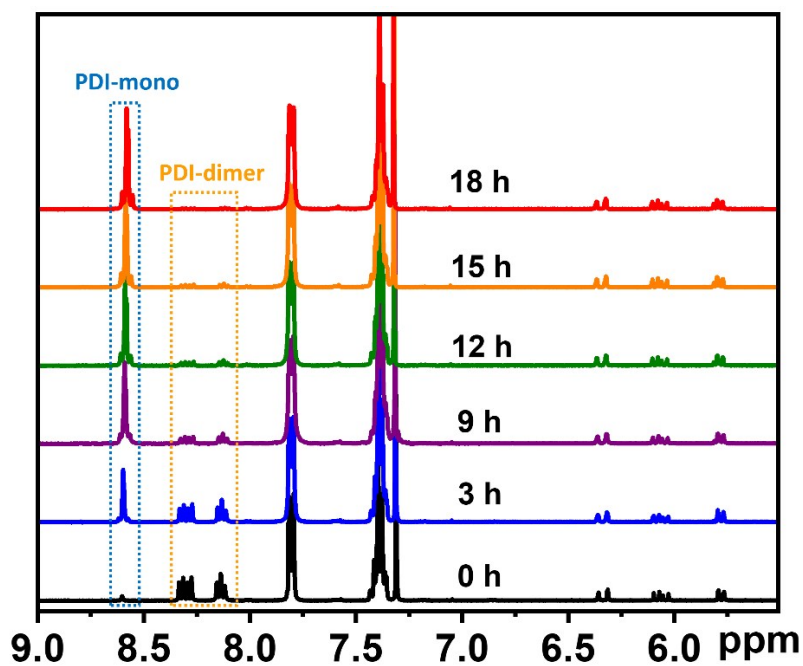
## 2. $^1\text{H}$ NMR spectra during transesterification

Figure S1 shows the  $^1\text{H}$  NMR spectrum of PDI-dimer in  $\text{CDCl}_3$ . The resonance absorptions from 6.45 to 5.75 ppm are ascribed to the protons of vinyl groups. Moreover, a large chemical shift separation ( $\Delta\delta$ ) between  $\text{H}_a$  (outer protons) and  $\text{H}_b$  (inner protons) of perylene units, which is  $\Delta\delta = 0.22$ , is observed. It convinces that a typical folded structure is adopted in PDI-dimer.



**Figure S1.** Chemical structure of PDI-dimer and its <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>.

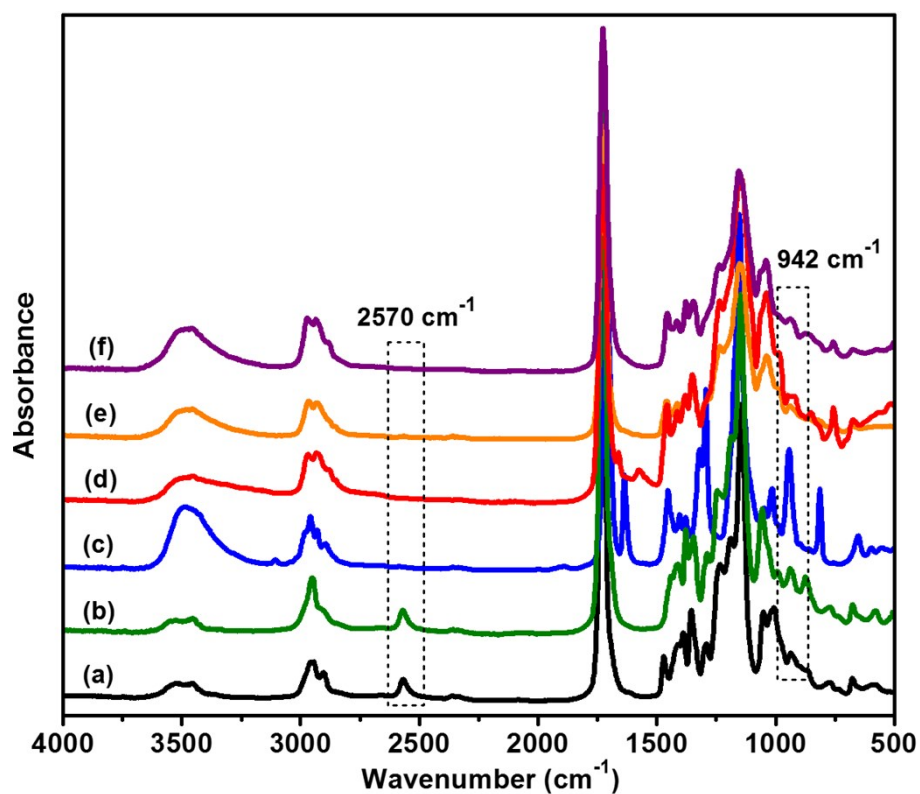
To a solution of PDI-dimer in CDCl<sub>3</sub> (1.0 mg/mL, 400 μL) was added the CD<sub>3</sub>OD solution of BSA (10 mg/mL, 100 μL, 26 eq. of PDI-dimer). The mixed solution was annealing at 60 °C for different times. <sup>1</sup>H NMR spectroscopy was used to monitor the transesterification process during thermal treatment. As shown in Figure S2, PDI-dimer presents a good folded structure before annealing with a larger chemical shift separation ( $\Delta\delta$ ) between H<sub>a</sub> (outer protons) and H<sub>b</sub> (inner protons) of perylene ranged from 8.45 to 8.05 ppm. During annealing, these characteristic resonance absorptions of perylene gradually decrease. Meanwhile, a new absorption peaked at around 8.60 ppm is observed with a smaller  $\Delta\delta = 0.09$ , which is ascribed to the unfolded structure as well as the free perylene unit. Moreover, other resonance absorptions are well kept and don't show obvious shift or decrease during annealing.



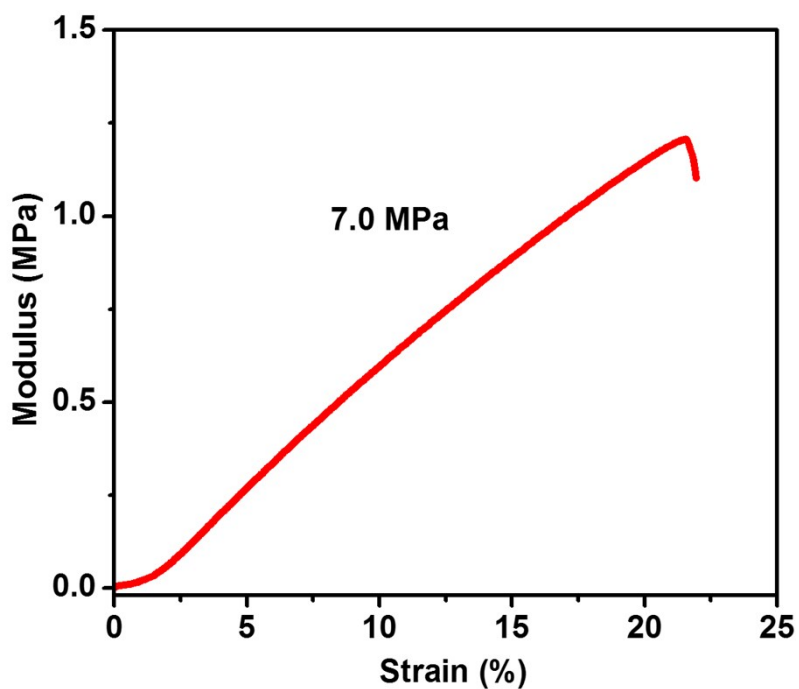
**Figure S2. <sup>1</sup>H NMR spectra in solution during annealing.** <sup>1</sup>H NMR spectra of the CDCl<sub>3</sub> solution of PDI-dimer in the presence of 26 eq. BSA and 20 vol% CD<sub>3</sub>OD before and after heating at 60 °C for different times.

### 3. Characterization of crosslinked TMN networks

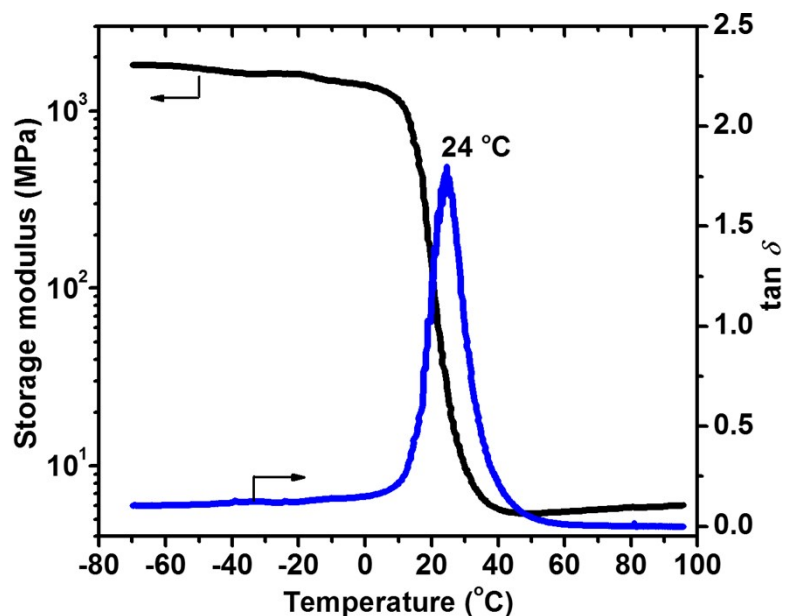
Complete consumption of thiols was verified by ATR-FTIR spectroscopy. As shown in Figure S3, the absorption peaks at 2570 and 942 cm<sup>-1</sup> can be ascribed to the stretching vibration of S-H and the bending vibration of CH<sub>2</sub>=C<, respectively. These two absorptions completely disappeared in cured TMN-TEA and TMN-TBD elastomers, suggesting the consumption of thiol and vinyl groups.



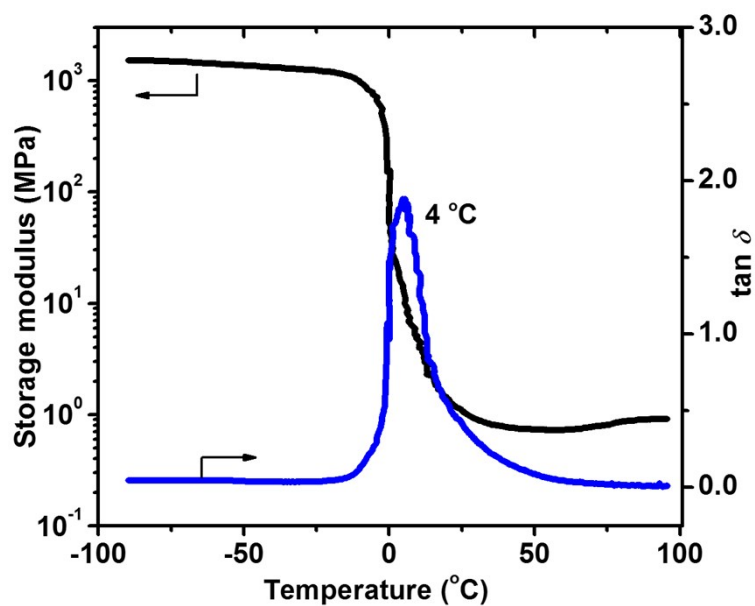
**Figure S3.** FTIR spectra of PTMP (a), EGBMP (b), GDMA (c), TMN100-TBD (d), TMN100-TEA (e), and TMN20-TEA (f) after curing.



**Figure S4.** Strain–stress curves recorded for TMN100-TBD elastomer.



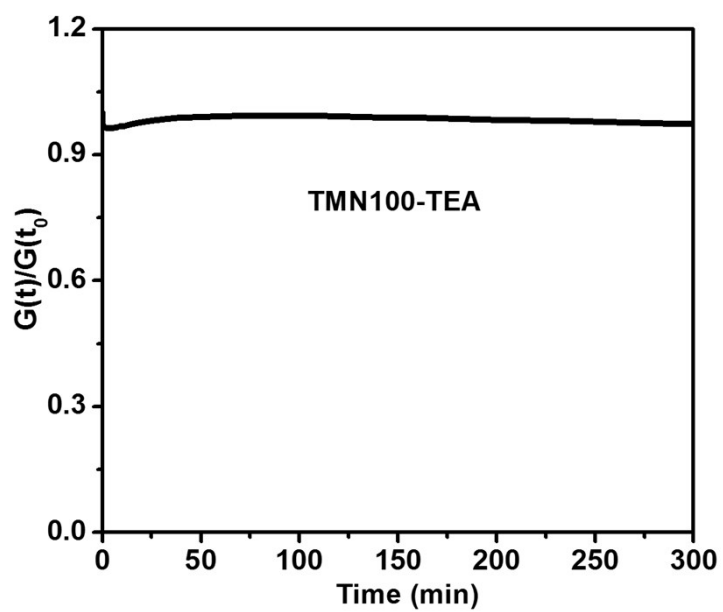
**Figure S5.** Dynamic mechanical analysis (DMA) of TMN100-TBD elastomer.



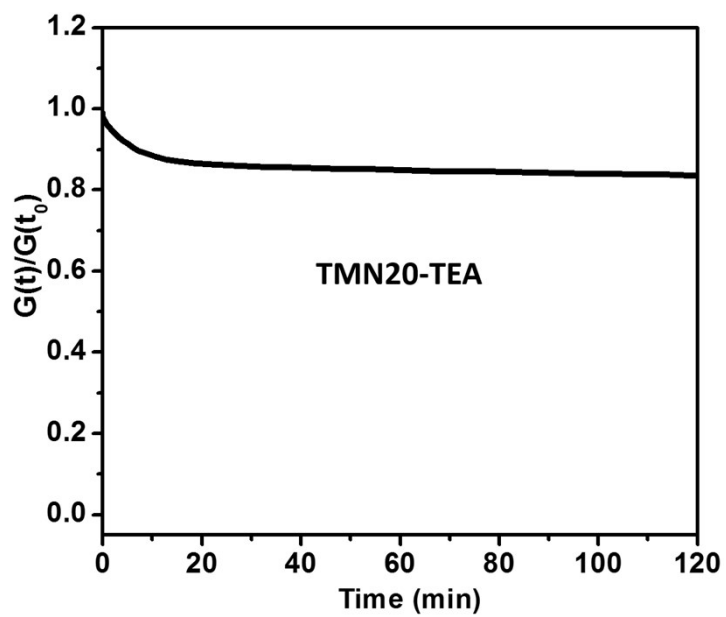
**Figure S6.** Dynamic mechanical analysis (DMA) of TMN20-TEA elastomer.

#### 4. Stress relaxation and fluorescent property of TMNx-TEA elastomer

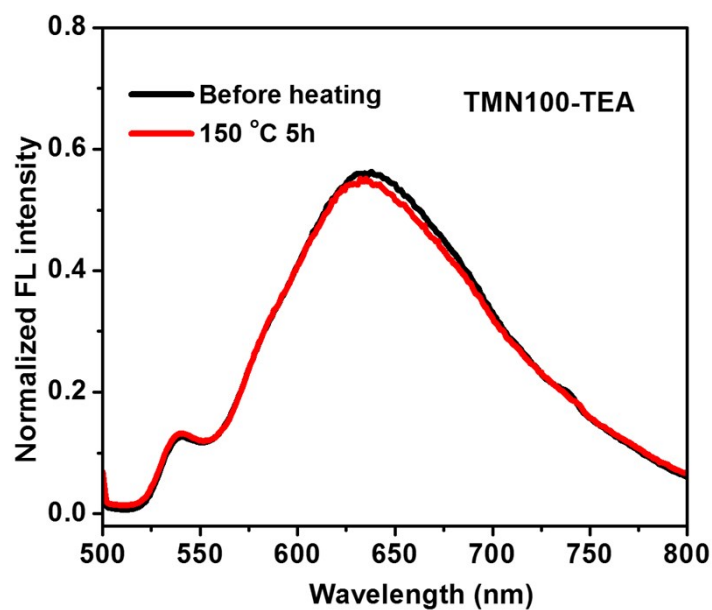
TEA is a good base catalyst for Thiol-Michael reaction. But it is unable to drive the transesterification. As shown in Figure S7 and S8, no obvious stress relaxation was observed during annealing for TMN100-TEA and TMN20-TEA. Meanwhile, their emission spectra don't show obvious change before and after thermal treatment as well (Figure S9 and S10). The results obtained from fluorescent spectra are in accordance with those from stress relaxation experiment.



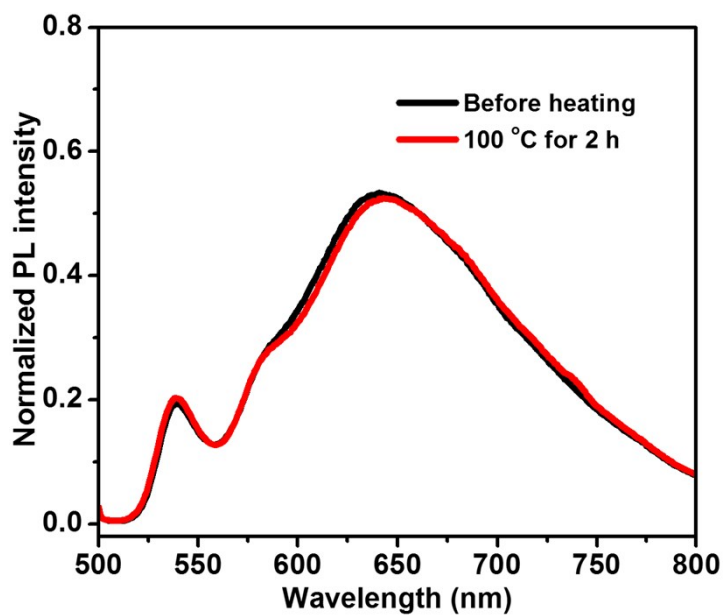
**Figure S7.** Stress relaxation of TMN100-TEA at 150 °C.



**Figure S8.** Stress relaxation of TMN20-TEA at 100 °C.



**Figure S9.** Normalized emission spectra of TMN100-TEA elastomer before and after stress relaxation at 150 °C for 5 h.

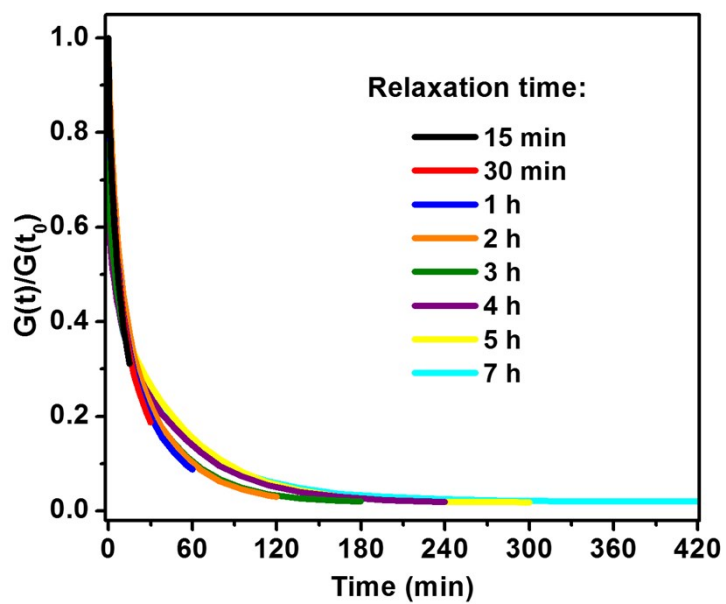


**Figure S10.** Normalized emission spectra of TMN20-TEA elastomer before and after stress relaxation at 100 °C for 2 h.

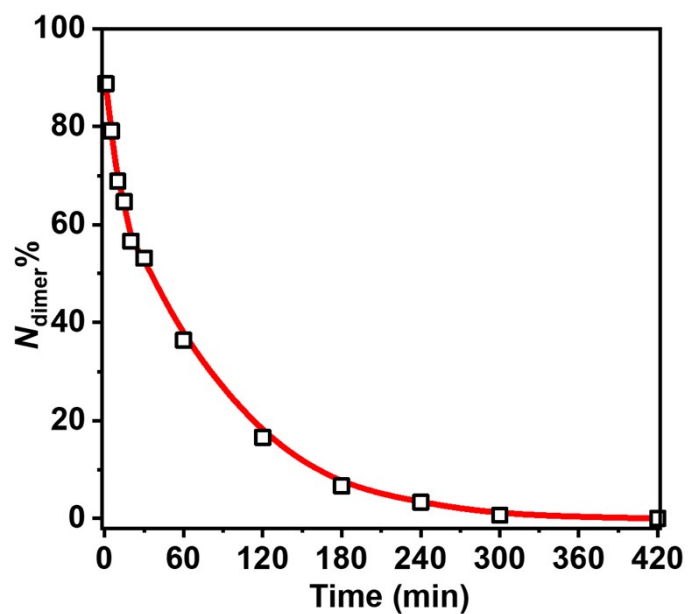
## 5. Stress relaxation and fluorescent property of TMN100-TBD elastomer

PL spectroscopy was used to trace the stress relaxation process. The relaxation experiment was stopped at different times and the sample after annealing was sent to test the emission spectra.

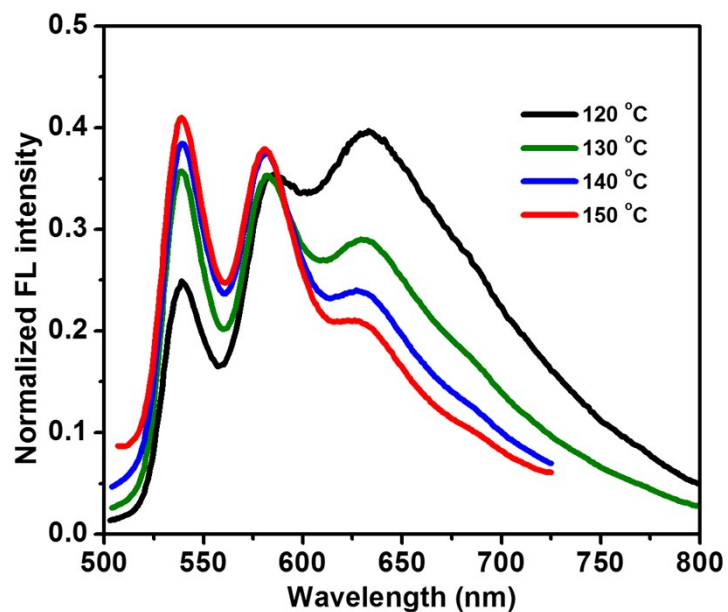




**Figure S11.** Stress relaxation of TMN100-TBD at 150 °C with different relaxation times.

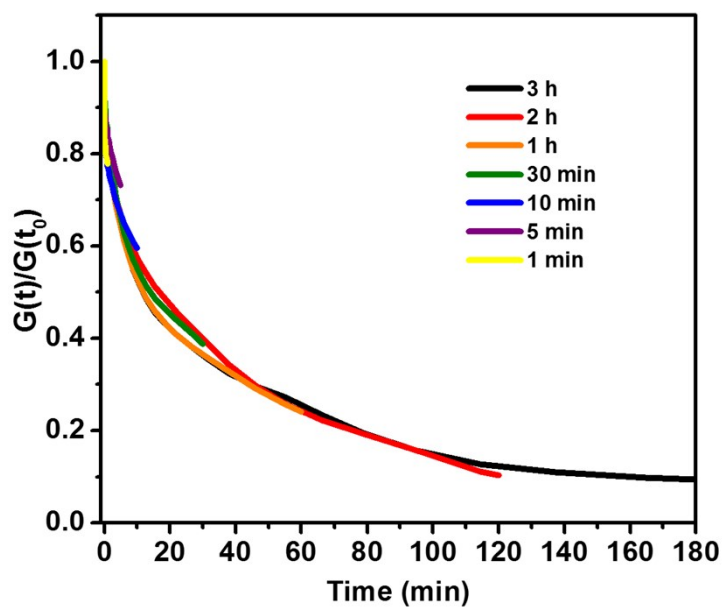


**Figure S12.**  $N_{dimer}\%$  changed with relaxation time for TMN100-TBD.

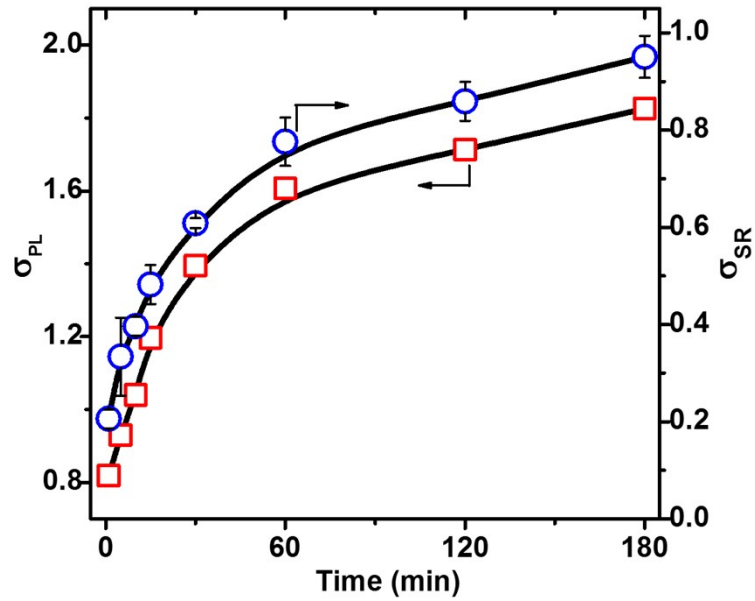


**Figure S13.** Normalized emission spectra of TMN100-TBD elastomer after stress relaxation at different temperatures for 5 h.

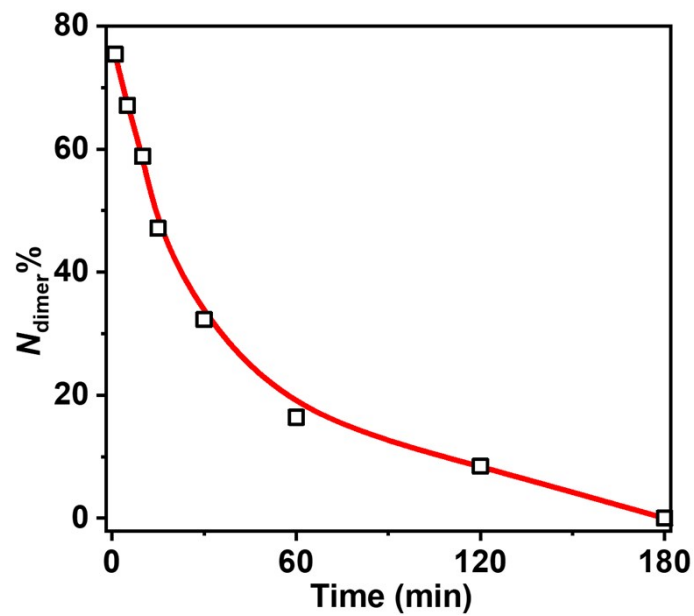
#### 6. Stress relaxation and fluorescent property of TMN20-BSA elastomer



**Figure S14.** Stress relaxation of TMN20-BSA elastomer with different relaxation times.



**Figure S15.**  $\sigma_{PL}$  and  $\sigma_{SR}$  of TMN20-BSA changed with relaxation time. Annealing temperature: 100 °C.

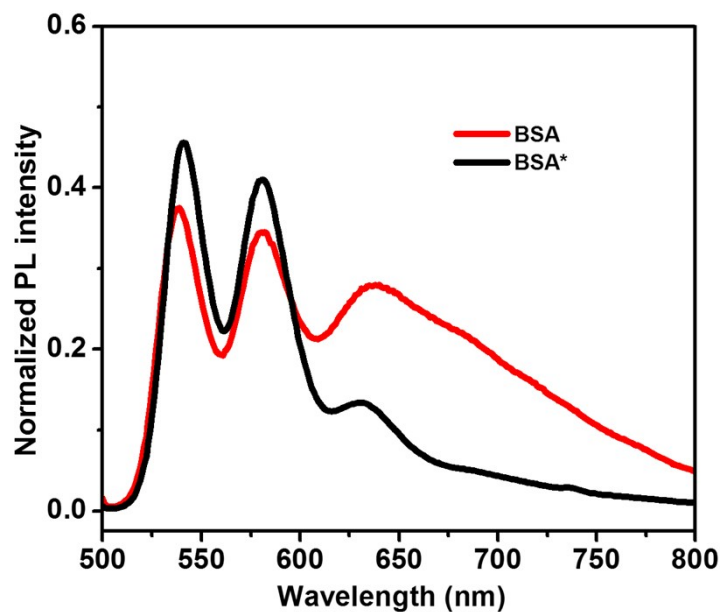


**Figure S16.**  $N_{dimer}\%$  changed with relaxation time for TMN20-BSA.

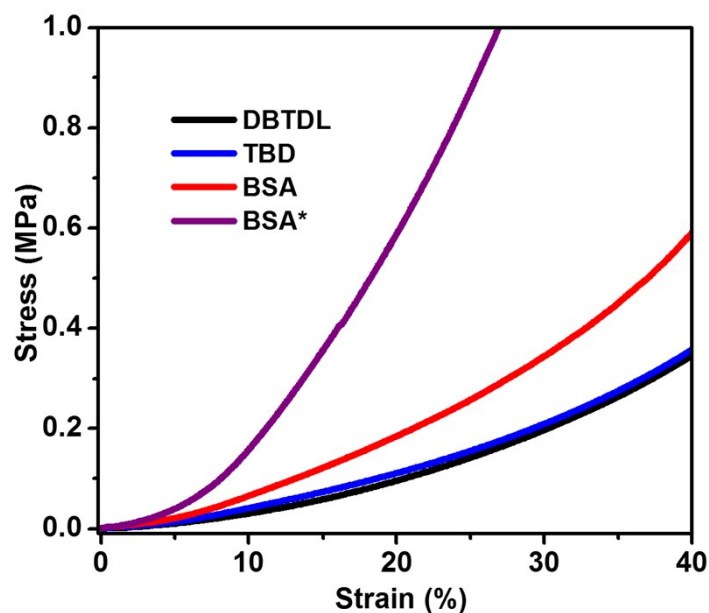
## 7. Fluorescent property and strain-stress curves of PHBA elastomer before and after thermal treatment

BSA is a highly efficient transesterification, which can activate bond exchange at lower temperature compared to other catalysts. During free radical polymerization, non-equilibrium transesterification has been driven by BSA leading to the transition from PDI-dimer to free PDI units (Figure S17).

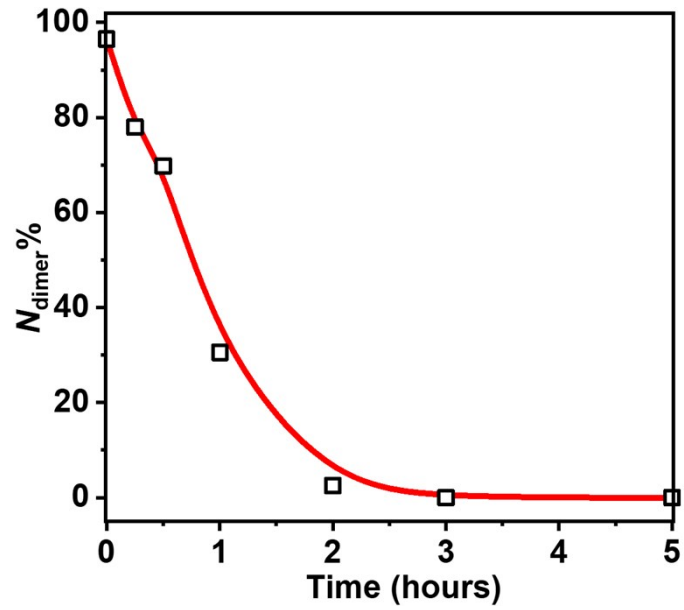
This nonequilibrium transesterification also can be evinced from the increased modulus (Figure S18). The higher the extent of nonequilibrium transesterification, the higher the modulus of as-prepared elastomer.



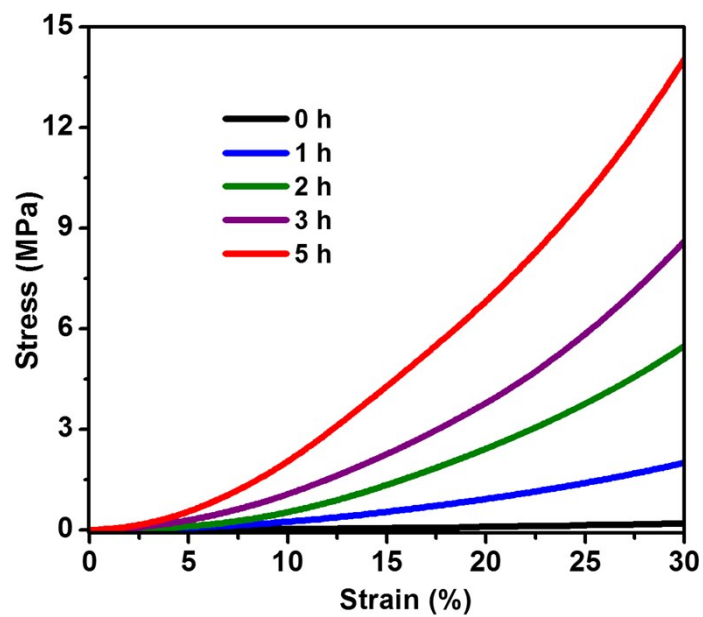
**Figure S17.** Normalized emission spectra of PHBA-BSA and PHBA-BSA\* elastomer after polymerization. The content of BSA is 0.2 mol% and 0.6 mol% for TMN-BSA and PHBA-BSA\*, respectively.



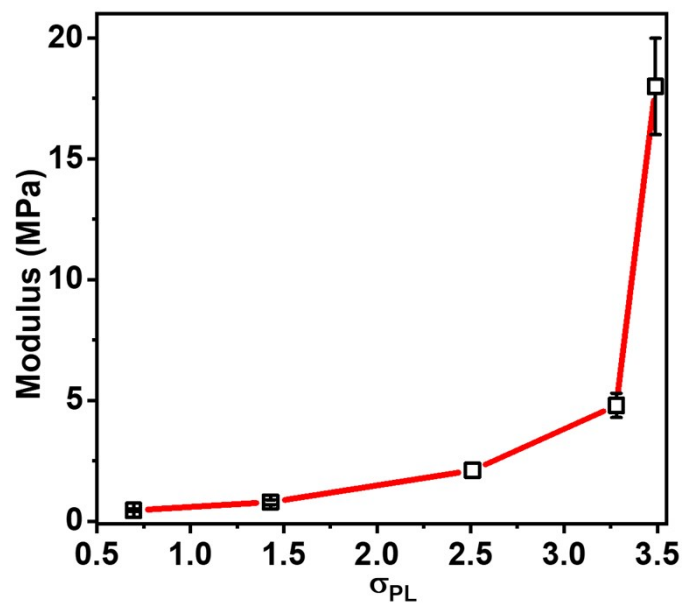
**Figure S18.** Strain–stress curves recorded for PHBA-DBTDL, PHBA-TBD, PHBA-BSA, and PHBA-BSA\* elastomer. Content of transesterification catalyst: 0.2 mol% for BSA, TBD, DBTDL, and 0.6 mol% for BSA\*.



**Figure S19.**  $N_{\text{dimer}}\%$  of crosslinked PHBA elastomer containing 0.2 mol% DBTDL during annealing at 150 °C for different times.

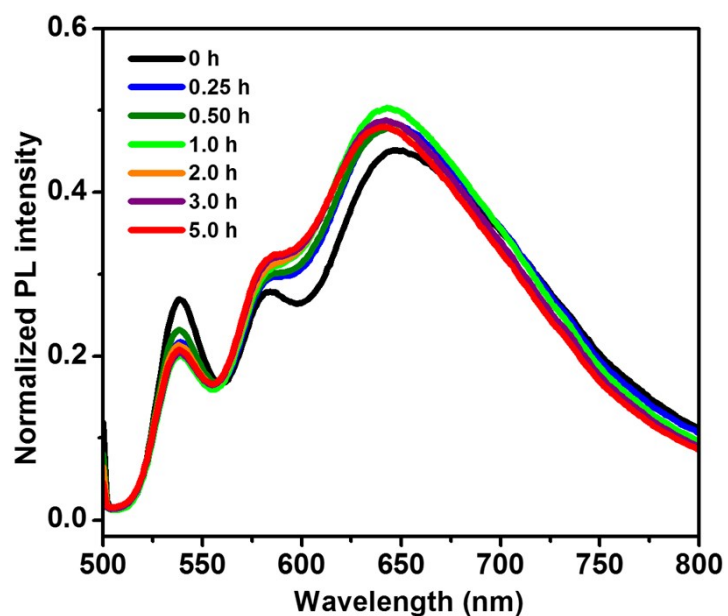


**Figure S20.** Strain–stress curves recorded for crosslinked PHBA elastomer containing 0.2 mol% DBTDL during annealing at 150 °C for different times.

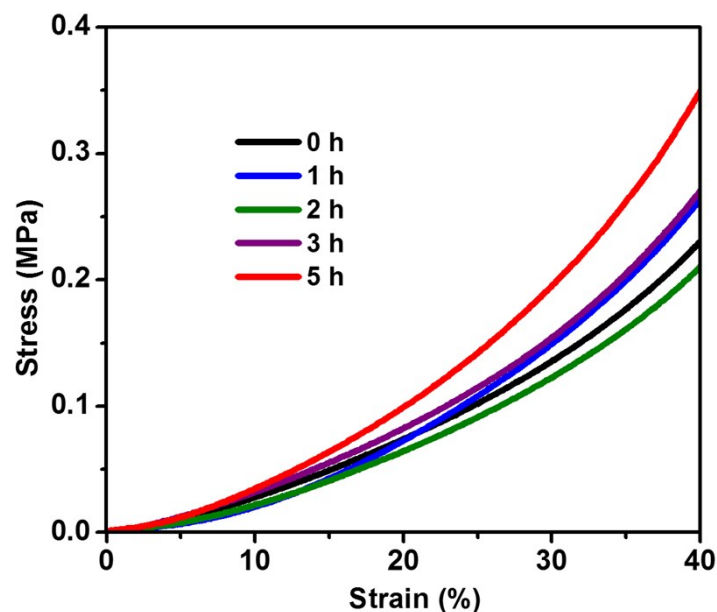


**Figure S21.** The quantitative relationship between modulus and  $\sigma_{PL}$  for PHBA-DBTDL during the stiffening process.

Without any transesterification, the PHBA kept the PDI-dimer structure very well during thermal treatment. No obvious changes are observed in emission spectra (Figure S22).



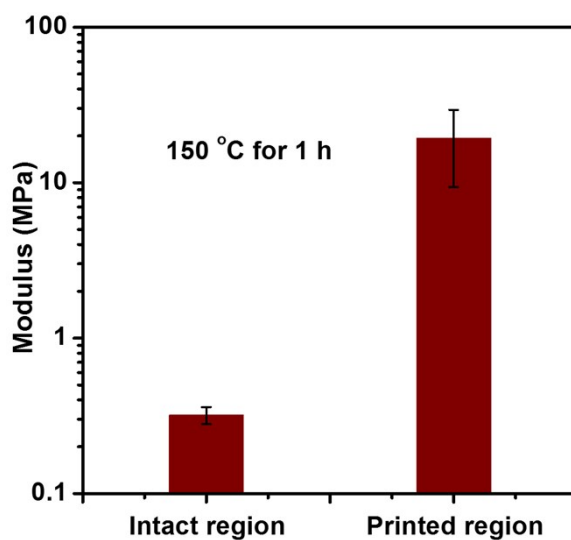
**Figure S22.** Normalized PL spectra of crosslinked PHBA elastomer containing no transesterification catalyst during heating at 150 °C for different times.



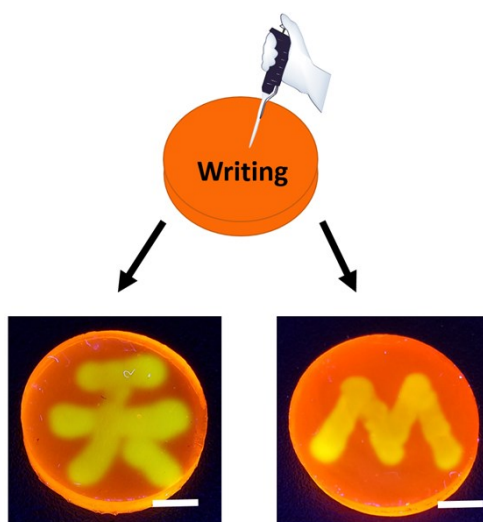
**Figure S23.** Strain–stress curves recorded for crosslinked PHBA elastomer containing no transesterification catalyst during annealing at 150 °C for different times.

## 8. Spatiotemporal self-report of transesterification

The PHBA sample was prepared via AIBN-initiated free radical polymerization without addition of any transesterification catalyst. After polymerization, the as-prepared sample exhibited orange fluorescent owing to the folded PDI-dimer structure. Then the ethanol solution of BSA (20 mg/mL) were printed on the targeted areas. Before thermal treatment, no obvious fluorescent color change was obvious. But after annealing at 80 °C for 8.0 h or 150 °C for 1.0 h, the regions containing BSA displayed the bright yellow emission, implying the transition from dimerized PDI state to monomeric state. At the meantime, we tested the modulus via instrumented indenter (FISCHERSCOPE HM2000) using a spherical-conical diamond indenter. As shown in Figure 5d and S24, the regions with BSA display apparently higher modulus after annealing. This stiffening was ascribed to the non-equilibrium transesterification process. Higher annealing temperature engenders higher modulus. The difference between regions with and without BSA in mechanical property evinces the difference in fluorescent color stems from transesterification. Thereby, the spatiotemporal bond exchange also can be successfully visualized.

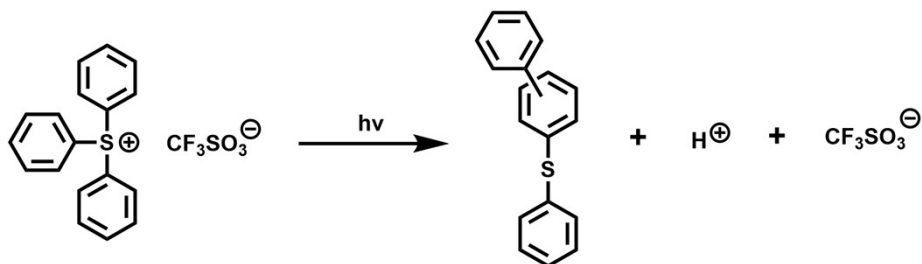


**Figure S24.** Modulus of the intact and printed regions after annealing at 150 °C.



**Figure S25.** Site-specifically writing the ethanol solution of catalyst (BSA, 20 mg/mL) on the targeted areas of PHBA materials followed by annealing at 80 °C for 8 h.

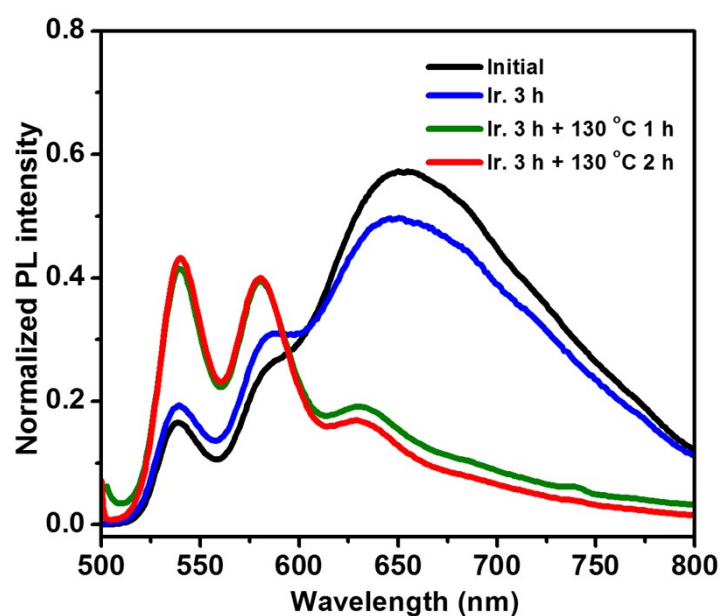
### 9. Visualized spatial transesterification controlled via light



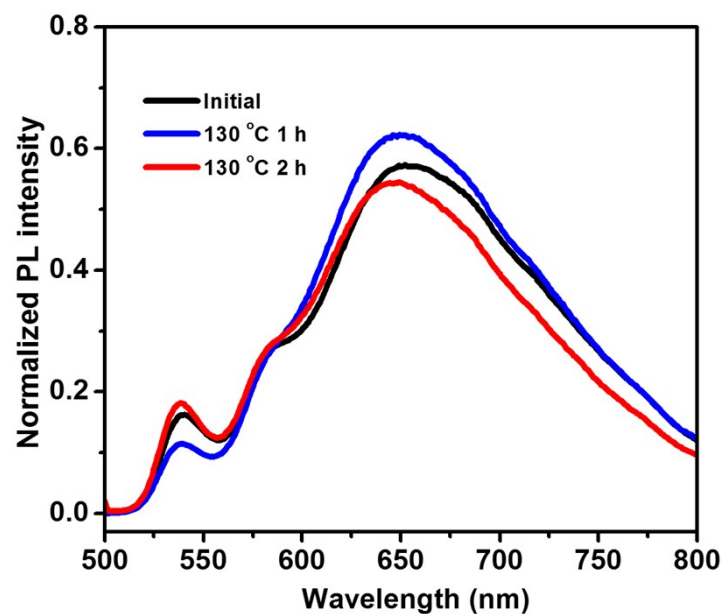
**Scheme S1.** The photolysis of triphenylsulfonium triflate (TPST).



Note that light takes advantage of spatiotemporal control and constitute powerful tool in various applications. Here, we also use light to control the transesterification areas. Triphenylsulfonium triflate (TPST) was chosen as the photo-acid generator. It could produce the common strong Brønsted acid (triflic acid) under 254 nm UV light (Scheme S1), which can serve as the transesterification catalyst.<sup>1,2</sup> TPST was added to the monomer solution, then the mixture was sent to free radical polymerization to obtain PHBA elastomer (PHBA-TPST). The as-prepared PHBA-TPST kept the dimerized PDI-structure judged from its orange fluorescence (Figures S26 and S27). If the PHBA-TPST was sent to anneal at 130 °C without irradiation treatment, the emission spectra don't show any obvious changes (Figure S27). In contrast, after irradiation under 256 nm UV light for 3 h, the elastomer still maintained the initial orange emission, but it would quickly transfer to the yellow fluorescence upon heating at 130 °C (Figure S26), attributed to the transesterification triggered by triflic acid released by TPST during irradiation. Then we can control the transesterification regions by using different photomasks to get various expected patterns (Figure 5d).



**Figure S26.** Normalized PL spectra of crosslinked PHBA elastomer containing 8.5 wt% TPST before and after irradiation (254 nm for 3 h) and thermal treatment (130 °C for different times).



**Figure S27.** Normalized PL spectra of crosslinked PHBA elastomer containing 8.5 wt% TPST before and after thermal treatment (130 °C for different times).

## 10. References

1. Potje-Kamloth, K., Polk, B. J., Josowicz, M. & Janata, J. Doping of polyaniline in the solid state with photogenerated triflic acid. *Chem. Mater.* **14**, 2782-2787 (2002).
2. Self, J. L., Dolinski, N. D., Zayas, M. S., Read de Alaniz, J. & Bates, C. M. Brønsted-acid-catalyzed exchange in polyester dynamic covalent networks. *ACS Macro Lett.* **7**, 817-821 (2018).