# Supporting Information

# Integrated design of high-performance, recycling, and antibacterial 3D-printing photopolymers from tannic acid

Yuxuan Que[a,†], Hang Zhou[a,†], Tianyi Tang[b], Xuehan Chen[a,], Ying Li[a], Yi Tan*[a], Zhengchun Cai[a], Yuanyuan Jiang[b], Jianfeng Yao[a], Ping Zhao[c], Chengguo Liu*[a, c]

† These Authors contributed equally to this work

*Corresponding authors: Yi Tan, tanyi0906@163.com; Chengguo Liu, liuchengguo@njfu.edu.cn

This PDF file includes:

Supplementary Tables S1 to S14

Supplementary Figures S1 to S12

## S1. Experimental Section

*Materials:* Tannic acid (TA, analytical grade), isocyanatoethyl methacrylate (ICEMA, >99%), tetrahydrofurfuryl methacrylate (THFMA, >96%), dibutyltin dilaurate (DBTDL, >95%), and 2-hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173) were also supplied by Aladdin Co., Ltd. (China). Acetone (≥99.5%) was obtained from Nanjing Reagent Co., Ltd. (China) and used as the reaction solvent. ICEMA and THFMA were dried over molecular sieves for one week to remove trace moisture before use. All other reagents were used as received without further purification unless otherwise stated.

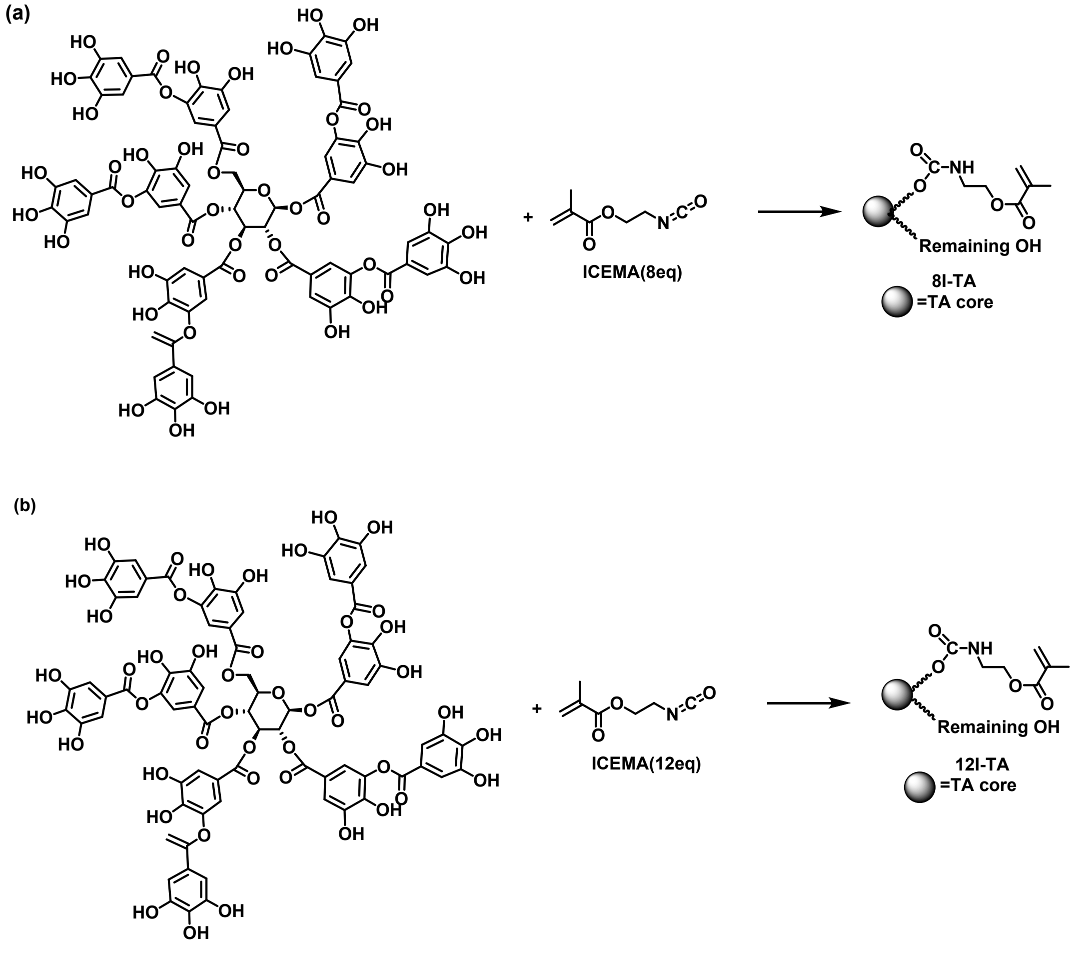

**Fig. S1** Synthetic route of 8I-TA (a) and 12I-TA (b).

*Synthesis of TA-based prepolymers*: The TA -based photosensitive prepolymers were synthesized *via* an isocyanate addition reaction, as schematically illustrated in Fig. S1. Typically, TA (17.01 g, 0.01 mol) and ICEMA were charged into a 250 mL fourneck round-bottom flask using acetone (150 mL) as solvent. For the preparation of the 8-functional prepolymer (8I-TA), ICEMA (12.40 g, 0.08 mol) was added, while for the 12-functional prepolymer (12I-TA), ICEMA (18.60 g, 0.12 mol) was used. The mixture was stirred under a nitrogen atmosphere and heated to 50°C. Subsequently, DBTDL (0.1 wt% relative to the total monomer mass) was added as the catalyst, and the reaction was allowed to proceed for 5 h. After completion, the reaction mixture was directly concentrated by rotary evaporation to remove acetone, affording the TA-based ICEMA-functionalized prepolymers with theoretical functionalities of 8 and 12, respectively. The obtained prepolymers were used for subsequent resin formulation without further purification.

*Preparation of UV-curing 3D printing TA-based resins*: UV-curable 3D printing resins were prepared by blending the synthesized TA-based ICEMA-modified prepolymers $(8\text{I-TA})_m\text{T}_n$ or $(12\text{I-TA})_m\text{T}_n$ with THFMA as reactive diluent and Darocur 1173 as photoinitiator. The mass ratios of prepolymer to THFMA were fixed at 8:2, 7:3, and 6:4, corresponding to THFMA contents of 20%, 30%, and 40%, respectively. For clarity, the obtained resins were denoted as $(8\text{I-TA})_m\text{T}_n$ or $(12\text{I-TA})_m\text{T}_n$, where m and n represent the mass fractions of the prepolymer and THFMA, respectively (e.g., $(12\text{I-TA})_6\text{T}_4$ represents a resin composed of 60 wt% (12I-TA) prepolymer and 40 wt% THFMA). Darocur 1173 was added at 2 wt% relative to the total mass of prepolymer and diluent. The mixtures were stirred at room temperature for 5 min until homogeneous and subsequently degassed under vacuum for 30 min to remove trapped air bubbles. For material characterization, the liquid resins were poured into polytetrafluoroethylene (PTFE) molds of designated shapes and cured under UV irradiation using a UV curing system (Intelli-Ray 400, Uvitron International Corporation, USA) equipped with a 365 nm light source at an intensity of 100 W cm$^{-2}$ for 600 s. For digital light processing (DLP)-based 3D printing, the formulated liquid resins were loaded into a Photon Ultra DLP printer (Anycubic Corporation, China). The printing models were pre-processed and sliced using Photon Workshop software. The layer thickness was set to 15 μm, and the exposure time for each layer was 7 s. After printing, the as-printed objects were rinsed thoroughly with ethanol to remove uncured resin on the surface and then post-cured for 300 s in a UV curing chamber (HTBX-II, Height-LED Corporation, China) under 365 nm UV light with an intensity of 100W cm$^{-2}$.

**Table S1** Compositions of 8I-TA and 12I-TA resins

| **Sample** | **TA (g)** | **ICEMA (g)** | **THFMA* (g)** | **Darocur 1173 (g)** |
|---|---|---|---|---|
| $(8I\text{-}TA)_8T_2$ | 17.01 | 12.40 | 7.35 | 0.74 |
| $(8I\text{-}TA)_7T_3$ | 17.01 | 12.40 | 12.60 | 0.84 |
| $(8I\text{-}TA)_6T_4$ | 17.01 | 12.40 | 19.60 | 0.98 |
| $(12I\text{-}TA)_8T_2$ | 17.01 | 18.60 | 8.90 | 0.89 |
| $(12I\text{-}TA)_7T_3$ | 17.01 | 18.60 | 15.26 | 1.02 |
| $(12I\text{-}TA)_6T_4$ | 17.01 | 18.60 | 23.74 | 1.2 |

*THFMA: tetrahydrofurfuryl methacrylate.

*Recycling of cured biobased resins*: To evaluate the recyclability of the TA–based UV-cured resins, a mixed-monomer assisted recycling strategy was adopted. Typically, 2.0 g of the cured $(12I\text{-}TA)_6T_4$ specimen was placed into a 25 mL three-neck round-bottom flask. Subsequently, ICEMA (8.0 g) and THFMA (5.33 g) were added into the flask, and the mixture was stirred at 140°C under a nitrogen atmosphere. The solid sample gradually softened and dissolved within 2 h, yielding a homogeneous liquid system. After the degradation–reconstruction process, fresh TA (3.0 g) was introduced to react with the residual isocyanate groups, thereby restoring the dynamic network structure and obtaining a recyclable, photo-curable resin. The mass fraction of THFMA in the recovered resin was maintained at a level comparable to that of the original formulation to ensure consistency in processing behavior and material properties. The recycled resin was subsequently used for re-curing and further characterization.

*Characterization*: FT-IR spectra were obtained using a Nicolet iS10 infrared spectrometer (Thermo-Fisher Scientific, USA) over the range of 4000–500 cm$^{-1}$ with a resolution of 4 cm$^{-1}$, Real-time infrared (RT-IR) measurements were carried out on a modified Nicolet 5700 spectrometer (Thermo-Nicolet, USA) under a UV exposure intensity of 100 W cm$^{-2}$, and the polymerization kinetics were analyzed by monitoring the absorption band at 810 cm$^{-1}$. Gel contents were determined *via* Soxhlet extraction, and volumetric shrinkage was measured using an FZMD-2 electronic densitometer (Shanghai Fangrui Corporation, China) according to the same methods. Dynamic mechanical analysis (DMA) was performed on a Q800 dynamic mechanical analyzer (TA Instruments, USA) in tensile mode at a frequency of 1 Hz over a temperature range from −50 to 220°C for the recycled resins and from −50 to 180°C for the 8I-TA resins and from -50 to 150°C for the 12I-TA resins, with a heating rate of 5°C min$^{-1}$. Thermogravimetric analysis (TGA) was conducted using an STA 409PC thermal analyzer (Netzsch, Germany) under a nitrogen atmosphere, where the cured samples were ground into powders and approximately 10 mg of material was heated from 35 to 700 °C at a rate of 20 °C min$^{-1}$. Tensile properties were measured using an SANS CMT-4304 universal testing machine (Shenzhen Xinsansi Jiliang Instrument Corporation, China) at a speed of 5.0 mm min$^{-1}$ and a gauge length of 40 mm, and the reported values represent the average of five specimens tested at room temperature. Molecular weight distributions were determined by gel permeation chromatography (GPC) using a Waters Alliance system equipped with a refractive index detector (Waters Corporation, USA) with tetrahydrofuran as the mobile phase at 35°C and a flow rate of 1.0 mL min$^{-1}$, where all samples were filtered through a 0.45 μm PTFE syringe filter prior to injection and calibrated using polystyrene standards. Antibacterial activity was evaluated in accordance with ISO 22196:2007 using circular $(12I\text{-}TA)_8T_2$, $(12I\text{-}TA)_7T_3$, and $(12I\text{-}TA)_6T_4$ films (40 mm in diameter) inoculated with *E. coli, S. aureus, and S. mutans* and incubated at 37°C, with colony-forming units quantified by the plate-count method.

## S2. Optimization of experimental conditions

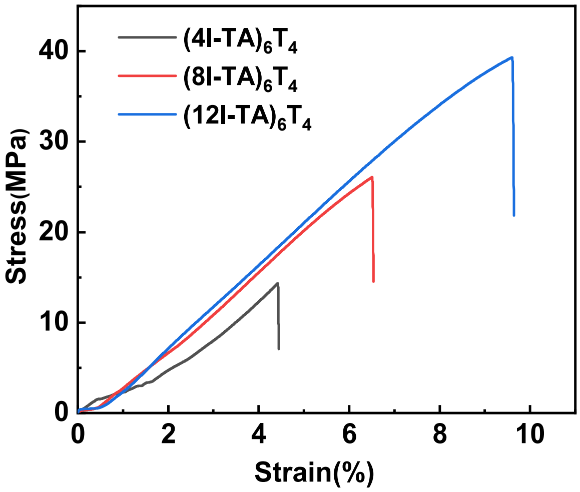

**Fig. S2** Stress–strain curves of TA-based resins synthesized with different ICEMA equivalents (4, 8, 12eq) at a fixed THFMA content.

## S3. Structural characterization

### S3.1 FT-IR characterization

FT-IR spectra of TA, $(8I\text{-}TA)_mT_n$, and $(12I\text{-}TA)_mT_n$ obtained by the reaction with ICEMA are shown in Fig. S3. Compared with pure TA, the absorption peaks of the –OH stretching vibration at approximately 3400 cm$^{-1}$ in the 8I-TA and 12I-TA were significantly weakened or even almost disappeared. This indicated that the phenolic hydroxyl group in the TA molecule was largely consumed during the reaction, confirming that it reacted effectively with the isocyanate group.

New absorption peaks appeared at 2915 and 2860 cm$^{-1}$ in the 8I-TA and 12I-TA, corresponding to the stretching vibrations of aliphatic –CH and –$CH_2$ groups. Compared with pure TA, the appearance and enhancement of these peaks indicated that the aliphatic segments introduced by the isocyanate reacted successfully onto the TA molecule and increased the number of methyl and methylene groups, leading to a significant enhancement of the C–H vibration signal. Furthermore, new absorption peaks appeared at 1705 and 1640 cm$^{-1}$ in the 8I-TA and 12I-TA, which can be attributed to the stretching vibration of C=O in the urethane structure and C=C in the methacrylate group, respectively. Simultaneously, the C–N stretching vibration absorption peak was observed at approximately 1320 cm$^{-1}$. These two characteristic peaks were typical markers of urethane bond formation, further demonstrating that the isocyanate group has reacted with the TA hydroxyl group and successfully constructed a modified TA system containing a urethane structure.

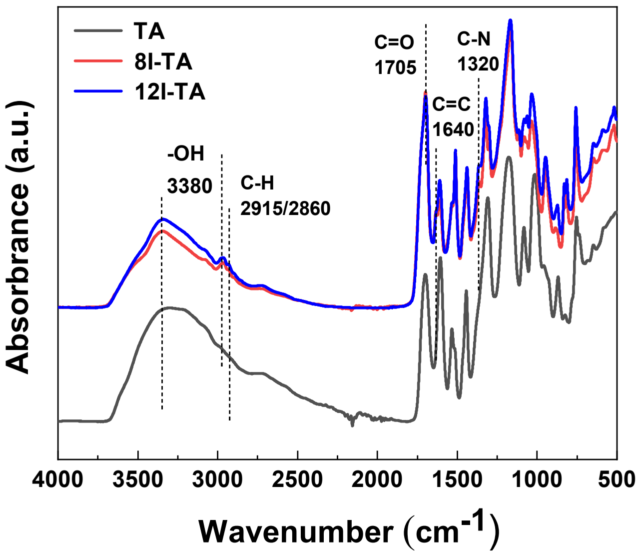

**Fig. S3** FT-IR spectra of TA, 8I-TA, and 12I-TA.

## S4. Physical properties and curing kinetic parameters

The gel content ($C_{\mathrm{gel}}$) of the cured samples was determined by solvent extraction and calculated using the following equation:

$$C_{gel}(\%) = (W_d/W_0) \times 100$$

where $W_0$ is the initial mass of the cured sample before solvent extraction, and $W_d$ is the mass of the sample after extraction and drying to constant weight.

The biobased content ($C_{\mathrm{bio}}$) of the resin system was calculated according to the mass fraction of the bio-based component in the formulation:

$$C_{bio}(\%) = (m_{bio}/m_{total}) \times 100$$

where $m_{bio}$ is the mass of the bio-based component (tannic acid, TA) in the formulation, and $m_{total}$ is the total mass of all components in the resin system.

The volumetric shrinkage ($\Delta V$) during photocuring was calculated based on the density change before and after curing:

$$\Delta V(\%) = 1 - (\rho_{uncured}/\rho_{cured}) \times 100$$

where $\rho_{uncured}$ is the density of the uncured resin and $\rho_{cured}$ is the density of the cured sample.

**Table S2** Physical properties and curing kinetic parameters of 8I-TA and 12I-TA

| **Sample** | $V_s$ [a] **(GPa·s)** | $C_{gel}$ [b] **(%)** | $C_{bio}$ [c] **(%)** | $C_{DCB}$ [d] **(mol/g)** | $\Delta V$ [e] **(%)** | $\alpha_f$ [f] **(%)** | $R_p$ [g] **($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| $(8I\text{-}TA)_8T_2$ | 12.2±0.1 | 93.3±0.2 | 58.3 | 0.00163 | 6.01±0.15 | 59.9 | 0.107 |
| $(8I\text{-}TA)_7T_3$ | 4.12±0.01 | 93.5±0.3 | 54.7 | 0.00190 | 7.71±0.25 | 59.5 | 0.099 |
| $(8I\text{-}TA)_6T_4$ | 2.60±0.01 | 95.2±0.1 | 50.4 | 0.00218 | 7.94±0.30 | 60.1 | 0.154 |
| $(12I\text{-}TA)_8T_2$ | 10.6±0.1 | 95.4±0.3 | 54.4 | 0.00202 | 6.92±0.25 | 64.3 | 0.098 |
| $(12I\text{-}TA)_7T_3$ | 3.02±0.01 | 95.9±0.2 | 50.7 | 0.00236 | 6.99±0.25 | 68.6 | 0.104 |
| $(12I\text{-}TA)_6T_4$ | 0.650±0.005 | 96.8±0.2 | 46.2 | 0.00270 | 7.13±0.30 | 72.2 | 0.090 |

[a] Viscosity at 25 °C. [b] Gel content. [c] Biobased content. [d] Content of dynamic covalent bond. [e] Volumetric shrinkage. [f] Final C=C conversion. [g] Maximum C=C conversion rate.

## S5. Photopolymerization kinetics curves of 8I-TA and 12I-TA resins

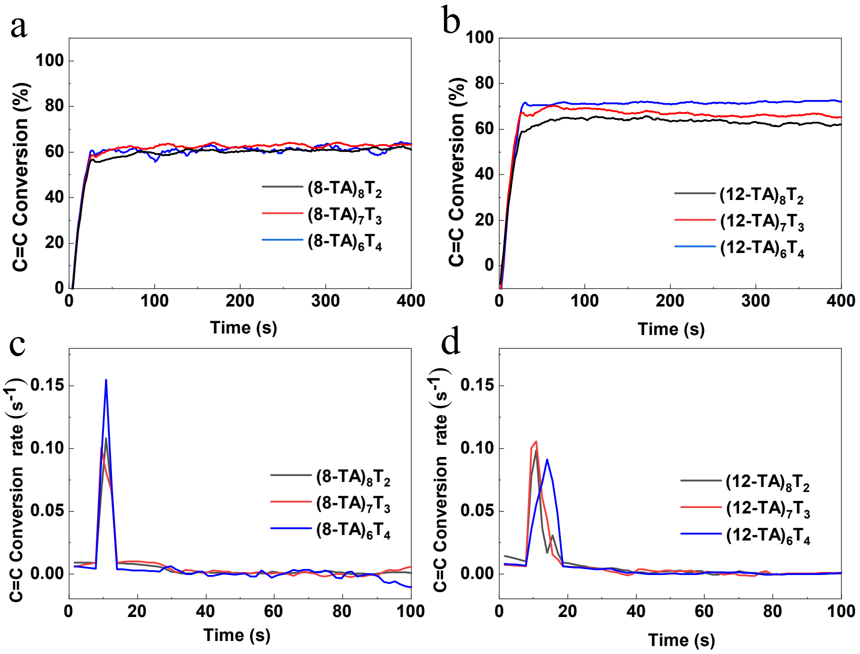

**Fig. S4** (a, b) C=C conversions and (c, d) their rates of 8I-TA and 12I-TA resins.

## S6. Thermal and mechanical properties of 8I-TA and 12I-TA resins

**Table S3** Thermal properties of 8I-TA and 12I-TA resins.

| Sample | $C_{HS}$ [a] (%) | $E'_{25}$ [b] (GPa) | $T_g$ [c] (°C) | $E'_{Tg+40}$ [d] (MPa) | $v_e$ [e] ($10^3$mol/m$^3$) | $T_5$ [f] (°C ) | $T_{max1}$ [g] (°C ) | $T_{max2}$ [h] (°C ) | $w_{char}$ [i] (%) |
|---|---|---|---|---|---|---|---|---|---|
| (8I-TA)$_8$T$_2$ | 83.4 | 1.15 | 92.9 | 35.1 | 3.54 | 153.5 | 298.4 | 411.0 | 19.5 |
| (8I-TA)$_7$T$_3$ | 85.4 | 1.43 | 95.5 | 26.9 | 2.69 | 161.8 | 299.8 | 411.3 | 15.9 |
| (8I-TA)$_6$T$_4$ | 87.5 | 1.48 | 94.2 | 16.0 | 1.57 | 154.6 | 303.0 | 372.6 | 5.64 |
| (12I-TA)$_8$T$_2$ | 77.8 | 1.38 | 98.1 | 58.6 | 6.07 | 130.6 | 303.7 | 414.4 | 17.4 |
| (12I-TA)$_7$T$_3$ | 80.6 | 1.78 | 101.6 | 57.0 | 5.70 | 155.6 | 309.5 | 371.5 | 14.9 |
| (12I-TA)$_6$T$_4$ | 83.4 | 1.47 | 95.0 | 30.7 | 2.92 | 155.6 | 306.5 | 372.2 | 13.0 |

[a] Hard segment content. [b] Storage modulus at 25°C. [c] Glass transition temperature. [d] Storage modulus at $T_g$+ 40°C. [e] Cross-link density. [f] 5% weight loss temperature. [g, h] Maximum thermal decomposition temperatures. [i] Char yield.

**Table S4** Mechanical properties of 8I-TA and 12I-TA resins.

| Sample | $\sigma^a$(MPa) | $E^b$(GPa) | $\varepsilon^c$(%) |
|---|---|---|---|
| $(8I\text{-}TA)_8T_2$ | 15.1±1.5 | 0.262±0.010 | 5.5±0.8 |
| $(8I\text{-}TA)_7T_3$ | 21.5±2.5 | 0.389±0.015 | 5.9±0.8 |
| $(8I\text{-}TA)_6T_4$ | 25.6±2.1 | 0.449±0.018 | 12.6±1.1 |
| $(12I\text{-}TA)_8T_2$ | 17.5±2.0 | 0.269±0.017 | 6.4±0.8 |
| $(12I\text{-}TA)_7T_3$ | 25.4±2.1 | 0.302±0.029 | 7.9±1.0 |
| $(12I\text{-}TA)_6T_4$ | 39.1±2.9 | 0.468±0.033 | 9.6±1.1 |

[a] Tensile strength. [b] Tensile modulus. [c] Elongation at the break.

## S7. Stress relaxation behaviors of 8I-TA and 12I-TA resins.

**Table S5** Relaxation times of 8I-TA and 12I-TA resins.

| Sample | $\tau^{*a}$(min) |
|---|---|
| $(8I\text{-}TA)_8T_2$ | 8.19 |
| $(8I\text{-}TA)_7T_3$ | 6.27 |
| $(8I\text{-}TA)_6T_4$ | 4.03 |
| $(12I\text{-}TA)_8T_2$ | 4.87 |
| $(12I\text{-}TA)_7T_3$ | 4.58 |
| $(12I\text{-}TA)_6T_4$ | 5.45 |

[a] Relaxation time at 100 °C.

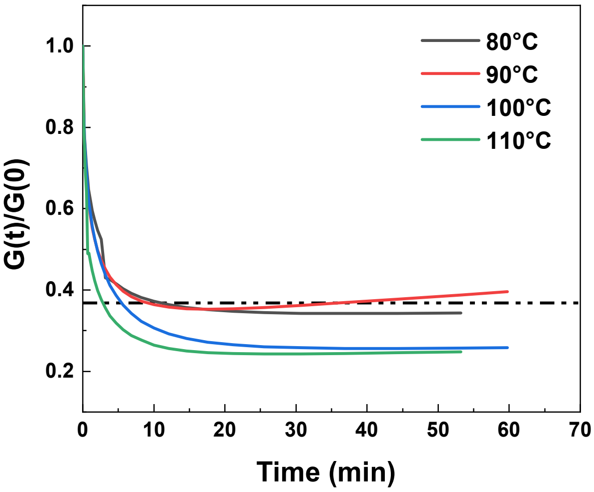

**Fig. S5** Stress relaxation curves of $(12I\text{-}TA)_6T_4$ at different temperatures.

**Table S6** $\tau^*$ of $(12I\text{-}TA)_6T_4$ at different temperatures.

| **Sample** | **$\tau^*$ (80°C) (min)** | **$\tau^*$ (90 °C) (min)** | **$\tau^*$ (100 °C) (min)** | **$\tau^*$ (110 °C) (min)** |
|---|---|---|---|---|
| $(12I\text{-}TA)_6T_4$ | 11.05 | 9.2 | 5.45 | 2.62 |

## S8. Thermal and mechanical properties of the recycled $(12I\text{-}TA)_6T_4$

**Table S7** Mechanical properties of the pristine and recycled $(12I\text{-}TA)_6T_4$.

| **Sample** | **$\sigma$ [a] (MPa)** | **$E$ [b] (GPa)** | **$\varepsilon$ [c] (%)** |
|---|---|---|---|
| Pristine | 39.1±2.9 | 0.468±0.033 | 9.6±1.12 |
| Cycle-1st | 51.9±1.8 | 0.586±0.026 | 8.1±0.45 |
| Cycle-2nd | 34.1±2.3 | 0.535±0.025 | 7.1±0.36 |
| Cycle-3rd | 28.1±1.7 | 0.430±0.021 | 7.8±0.53 |

[a] Tensile strength. [b] Tensile modulus. [c] Elongation at the break.

**Table S8** Thermal properties of the pristine and recycled $(12I\text{-}TA)_6T_4$.

| Sample | $E'_{25}$ [a] | $T_g$ [b] | $E'_{Tg+40}$ [c] | $\nu_e$ [d] | $T_5$ [e] | $T_{max1}$ [f] | $T_{max2}$ [g] | $w_{char}$ [h] |
|---|---|---|---|---|---|---|---|---|

|  | (GPa) | (°C) | (MPa) | ($10^3$mol/m$^3$) | (°C) | (°C) | (°C) | (%) |
|---|---|---|---|---|---|---|---|---|
| Pristine | 1.47 | 95.0 | 30.7 | 2.92 | 155.6 | 306.5 | 372.2 | 13.0 |
| Cycle-1st | 2.47 | 157.4 | 50.8 | 4.33 | 223.1 | 289.3 | 385.5 | 2.06 |
| Cycle-2nd | 1.68 | 152.3 | 33.6 | 2.89 | 205.1 | 287.2 | 385.7 | 4.65 |
| Cycle-3rd | 1.28 | 118.6 | 19.2 | 1.78 | 193.4 | 294.5 | 378.1 | 2.16 |

[a] Storage modulus at 25°C. [b] Glass transition temperature. [c] Storage modulus at $T_g$+ 40°C. [d] Cross-link density. [e] 5% weight loss temperature. [f, g] Maximum thermal decomposition temperatures. [h] Char yield.

To further evaluate the structural stability and integrity of the recycled networks, the swelling behavior of the original and recycled (12I-TA)$_6$T$_4$ samples was systematically investigated in solvents with different polarities, including $H_2O$, DCM, EA, EG, THF, PE, and DMF. The swelling ratio ($S$) was calculated according to the following equeation.

$$S = \left| \frac{W_t - W_0}{W_0} \right| \times 100\%$$

where ($W_0$) is the initial mass of the cured sample and ($W_t$) is the mass after immersion in solvent for 48 h following removal of residual surface solvent.

The corresponding swelling ratio results are summarized in Table S9, and the optical photographs before and after immersion are shown in Fig. S6. The original and recycled samples exhibited generally comparable swelling behavior and solvent resistance after multiple recycling cycles, indicating that the recycled networks largely maintained their crosslinked structure and structural stability during recycling. In DMF, all samples underwent complete disintegration during immersion because of the strong solvent penetration ability of DMF toward the dynamic polymer network, and therefore stable swelling ratio values could not be obtained.

**Table S9** Swelling ratios (%) of (12I-TA)$_6$T$_4$ and recycled resins after immersion in various solvents for 48 h

|  | $H_2O$ (%) | DCM (%) | EA (%) | EG (%) | THF (%) | PE (%) | DMF (%) |
|---|---|---|---|---|---|---|---|

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pristine | 4.33 | 24.6 | 0.89 | 0.78 | 7.1 | 0.04 | —— |
| Cycle-1st | 4.21 | 18.13 | 1.11 | 0.97 | 8.5 | 0.05 | —— |
| Cycle-2nd | 5.16 | 20.24 | 1.23 | 0.65 | 8.7 | 0.07 | —— |
| Cycle-3rd | 5.03 | 19.51 | 0.89 | 1.23 | 9.5 | 0.07 | —— |

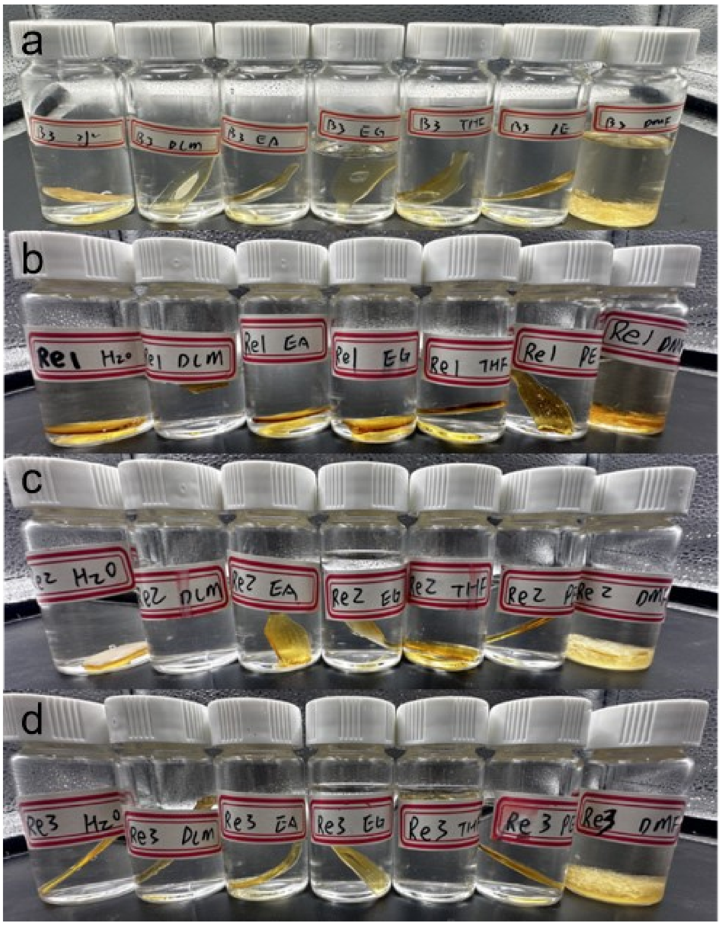

**Fig. S6** Photographs of $(12I\text{-}TA)_6T_4$(a) and recycled resins (b-d) after immersion in different solvents for 48 h

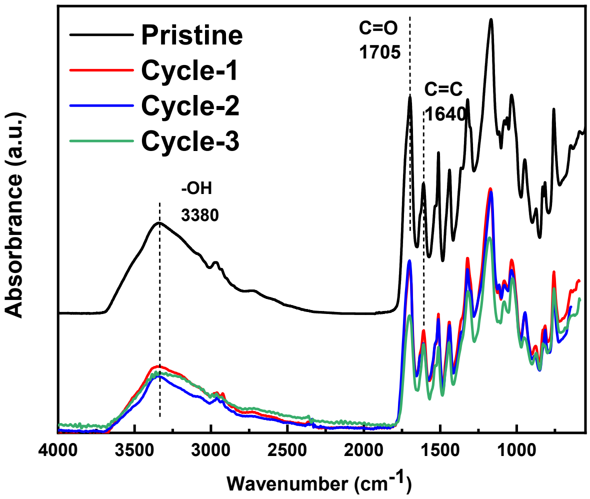

**Fig. S7** FT-IR spectra of Pristine and Cycled resins.

## S9. Photopolymerization behavior and printing feature-fidelity evaluation

The photopolymerization behavior of the resin was evaluated by measuring the cure depth ($Z_d$) under different exposure times using a DLP printer. The layer thickness was set to 0.02 mm, while the exposure times were adjusted to 28, 35, 42, 49, and 56 s, respectively. After exposure, the uncured resin was removed by solvent rinsing, and the thickness of the cured samples was measured using a digital micrometer. The measured thickness was defined as the $Z_d$. According to the Beer–Lambert law, the working curve can be expressed as:

$$Z_d = D_p ln\left(\frac{t}{t_c}\right)$$

where $Z_d$ is the cure depth, $D_p$ is the penetration depth, $t$ is the exposure time, and $t_c$ is the critical exposure time. $D_p$ and critical $t_c$ obtained from the linear fitting of $Z_d$ versus ln(t).

The fitting equation was determined to be:

$$Z_d = 0.0906 ln(t) - 0.134$$

Accordingly, $D_p$ and $t_c$ were calculated to be 90.6 μm and 4.39 s, respectively.

To further assess the printing feature fidelity, a dental model and fine structural features were printed under the same DLP conditions. The printed structures retained clear edges and continuous geometry without obvious collapse, merging, or distortion. Under the current printing conditions, the minimum distinguishable feature size was approximately 200 μm.

**Table S10.** Cure depth measurements used for working-curve analysis

| **$t$(s)** | **$ln$(t)** | **$Z_d$(mm)** |
|---|---|---|
| 28 | 3.332 | 0.168 |
| 35 | 3.555 | 0.188 |
| 42 | 3.378 | 0.205 |
| 49 | 3.892 | 0.220 |
| 56 | 4.025 | 0.231 |

**Table S11** Comprehensive comparison of $(12I\text{-}TA)_6T_4$ and petroleum-based commercial resin.

| **Sample** | **$\sigma$ [a] (MPa)** | **$E$ [b] (GPa)** | **$\varepsilon$ [c] (%)** | **$T_g$ [d] (°C)** | **$DC$ [e] (%)** | **$LT$ [f] (μm)** | **$E_c$ [g] (mJ/cm²)** | **$Vs$ [h] (mPa·s)** |
|---|---|---|---|---|---|---|---|---|
| $(12I\text{-}TA)_6T_4$ | 39.1 | 0.468 | 9.6 | 95 | 72.2 | 11.6 | 7 | 660 |
| Petroleum-based commercial resin | 20-50 | 0.5-1 | 3-25 | 60-90 | 60-75 | 10-25 | 10-25 | 200-1000 |

[a] Tensile strength. [b] Tensile modulus. [c] Elongation at the break. [d] Glass transition temperature. [e] Double bond conversion. [f] Layer thickness [g] Critical exposure energy. [h] Viscosity.

## S10. Antibacterial performance

### S10.1 Test of antibacterial performance of $(12I\text{-}TA)_mT_n$ resin against *Escherichia coli (E. coli)*

The antibacterial performance of the $(12I\text{-}TA)_mT_n$ resin against *E.coli* was quantitatively evaluated by a co-culture combined with a plate-counting method. In this test, the blank group referred to the bacterial suspension cultured without any sample.

### (1) Preparation of culture media

LB liquid medium was prepared by dissolving 2.5 g of LB broth in 100 mL of distilled water in a 250 mL bottle, followed by sterilization at 121°C for 15 min in an autoclave. The sterilized medium was then stored for later use.

LB agar medium was prepared by dissolving 2.5 g of LB broth and 1.5 g of agar powder in 100 mL of distilled water in a 250 mL bottle. After complete mixing, the medium was sterilized at 121°C for 15 min. The sterilized medium was cooled to approximately 40–50°C and then poured into sterile Petri dishes (15 mL per plate). For bacterial dilution, a 1/500 NB aqueous solution was prepared by dissolving 1.8 g of nutrient broth in 100 mL of distilled water and diluting it 500-fold with deionized water. The solution was sterilized at 115°C for 30 min and used as needed.

### (2) Preparation of bacterial suspension

Two sterile 12 mL culture tubes were prepared, each containing 3 mL of LB liquid medium. A single colony of *E. coli* was picked from an LB agar plate and inoculated into one tube, while the other tube was used as the blank culture control. The tubes were incubated in a shaking incubator at 37°C and 200 rpm overnight for 15 h. The bacterial suspension was then diluted with the 1/500 NB solution to a final concentration of $10^5$ CFU/mL.

### (3) Sample preparation

The test samples were placed in sterile disposable culture dishes and sterilized under UV light for 30 min before use. For the covering film, the film was cut into circular pieces with a diameter of 3 cm, soaked in ethanol for 1 h, and then air-dried before use.

### (4) Co-culture and plate-counting antibacterial test

A 150 μL aliquot of the diluted bacterial suspension ($10^5$ CFU/mL) was evenly dropped onto the sample surface. The sterilized covering film was placed over the sample using sterile tweezers to ensure uniform contact between the bacteria and the sample surface. Care was taken to prevent the bacterial suspension from flowing beyond the edge of the covering film. The samples were then incubated statically at 37°C for 24 h. After incubation, the bacterial suspension was recovered using 1.5 mL of sterile PBS. The recovered suspension was serially diluted 10-fold, and 100 μL of each dilution was spread onto LB agar plates. The plates were incubated at 37°C, and colonies were counted after 3 h, 12 h, and 24 h, respectively. The colony-counting principle followed GB 4789.2-2016. Only plates containing 30–300 CFU were used for statistical analysis. If no colonies were observed even at the lowest dilution, the antibacterial effect was considered pronounced.

**(5) Calculation of bacterial concentration and antibacterial rate**

The bacterial concentration (CFU/mL) was calculated using the following equation:

$$\text{CFU/mL} = \text{colony count} \times \text{dilution factor} \times 10 \times 10$$

where the first factor of 10 accounts for the recovery of bacteria from 150 μL of bacterial suspension into 1.5 mL sterile PBS, and the second factor of 10 accounts for plating 0.1 mL of the diluted suspension.

The antibacterial rate was calculated as follows:

$$\text{Antibacterial rate}(\%) = \left(1 - \frac{C_{\text{sample}}}{C_{\text{blank}}}\right) \times 100\%$$

Where $C_{\text{sample}}$ is the bacterial concentration recovered from the test sample and $C_{\text{blank}}$ is the bacterial concentration of the blank control group.

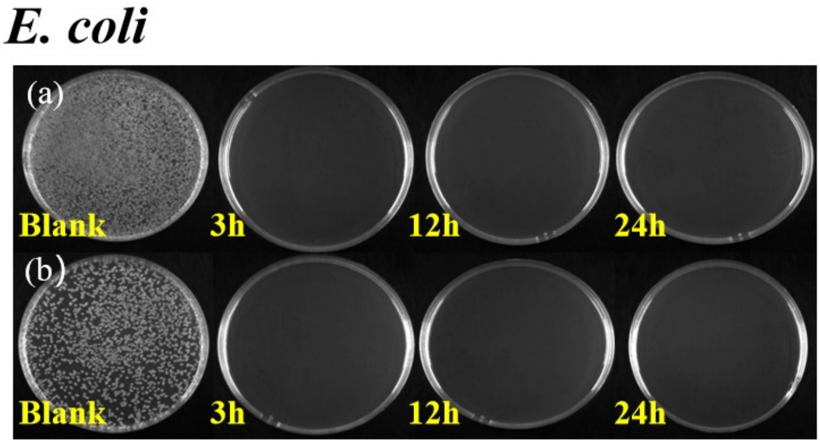

**Fig.S8** Antibacterial effect of $(12I\text{-}TA)_8T_2$ (a) and $(12I\text{-}TA)_7T_3$ (b) against *E.coli* in 3, 12, and 24 h, with the blank group as control.

**Table S12** Antibacterial performance of $(12I\text{-}TA)_mT_n$ resins against *E.coli* after 24 h

| Group | Colony count | Dilution factor | Bacterial concentration (CFU/mL) | Antibacterial rate |
|---|---|---|---|---|
| Blank | 260 | $10^3$ | $2.60\times10^7$ | |
| $(12I\text{-}TA)_8T_2$ | 0 | $10^1$ | $<1.00\times10^3$ | $>99.99\%$ |

| | | | | |
|---|---|---|---|---|
| (12I-TA)$_7$T$_3$ | 0 | $10^1$ | $<1.00\times10^3$ | $>99.99\%$ |
| (12I-TA)$_6$T$_4$ | 0 | $10^1$ | $<1.00\times10^3$ | $>99.99\%$ |

## S10.2 Test of antibacterial performance of (12I-TA)$_m$T$_n$ resin against *Streptococcus mutans (S.mutans)*

The antibacterial performance of (12I-TA)$_m$T$_n$ resin against *S.mutans* was quantitatively evaluated using a co-culture combined with a plate-counting method to simulate the direct contact process between bacteria and the material surface.

### (1) Preparation of culture media

The preparation procedure of the BHI liquid medium was the same as that described in Section S10.1, except that 2.5 g of LB broth powder was replaced with 3.85 g of BHI medium powder. The preparation procedure of the BHIA solid medium was also the same as that described in Section S10.1, except that 2.5 g of LB broth powder was replaced with 3.85 g of BHI medium powder.

### (2) Preparation of bacterial suspension

Two sterile 12 mL culture tubes were prepared, each containing 3 mL of BHI liquid medium. A single colony of *Streptococcus mutans* was picked from a solid agar plate and inoculated into one tube, while the other tube served as the blank control. The bacterial suspension was cultured overnight (15 h) in a thermostatic shaker at 37 °C and 200 rpm

### (3) Sample preparation

The samples were placed into sterile disposable culture dishes according to the experimental groups and sterilized under UV irradiation for 30 min before use.

### (4) Co-culture and plate-counting antibacterial test

The BHI liquid medium was diluted 500-fold with pure water, and the *Streptococcus mutans* suspension was further diluted to $10^5$ CFU/mL using the 1/500 BHI aqueous solution. Subsequently, 150 μL of the diluted bacterial suspension was evenly dropped onto the surface of each sample. A sterilized covering film was carefully placed onto the sample surface using sterile tweezers to ensure uniform contact between the bacteria and the sample surface, while preventing the bacterial suspension from overflowing beyond the edge of the covering film. The samples were then incubated statically at 37 °C for 24 h. After incubation, the bacteria were eluted using 1.5 mL sterile PBS solution. The recovered bacterial suspension was serially diluted by a factor of 10, and 100 μL of each diluted suspension was evenly spread onto BHIA solid medium plates. The plates were incubated at 37 °C for 3, 12, and 24 h, followed by photography and colony counting. The colony-counting principle, bacterial concentration calculation method (CFU/mL), and antibacterial-rate calculation were the same as those described for the antibacterial evaluation against *E. coli* in Section S10.1.

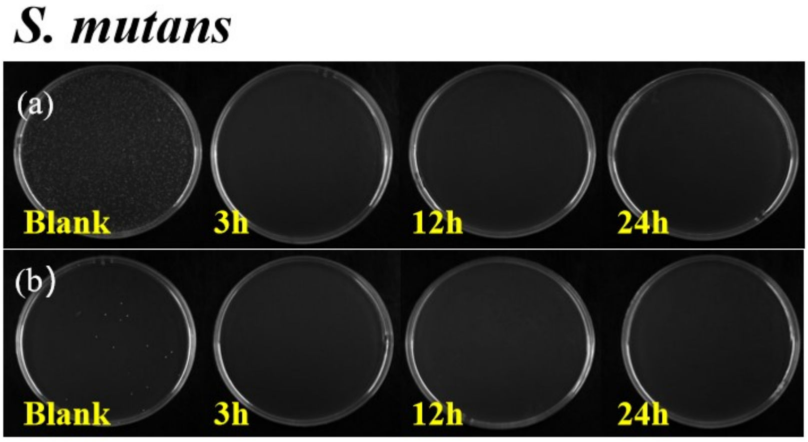

**Fig.S9** Antibacterial effect of (12I-TA)$_8$T$_2$ (a) and (12I-TA)$_7$T$_3$ (b) against *S.mutans* in 3, 12, and 24 h, with the blank group as control.

**Table S13** Antibacterial performance of (12I-TA)$_m$T$_n$ resins against *S.mutans* after 24 h

| Group | Colony count | Dilution factor | Bacterial concentration (CFU/mL) | Antibacterial rate |
|---|---|---|---|---|
| Blank | 275 | $10^3$ | $2.60\times10^7$ | |
| (12I-TA)$_8$T$_2$ | 0 | $10^0$ | $<1.00\times10^2$ | >99.96% |
| (12I-TA)$_7$T$_3$ | 0 | $10^0$ | $<1.00\times10^2$ | >99.96% |
| (12I-TA)$_6$T$_4$ | 0 | $10^0$ | $<1.00\times10^2$ | >99.96% |

### S10.3 Test of antibacterial performance of (12I-TA)$_m$T$_n$ resin against *Staphylococcus aureus (S.aureus )*

The antibacterial performance of (12I-TA)$_m$T$_n$ resin against *Staphylococcus aureus* was quantitatively evaluated using a co-culture combined with a plate-counting method to simulate the direct contact process between bacteria and the material surface.

**(1) Preparation of culture media**

The preparation procedures of the LB liquid medium, LB solid medium, and 1/500 NB aqueous solution were the same as those described in Section S10.1.

**(2) Preparation of bacterial suspension**

Two sterile 12 mL culture tubes were prepared, each containing 3 mL of LB liquid medium. A single colony of Staphylococcus aureus was picked from a solid agar plate and inoculated into one tube, while the other tube served as the blank control. The bacterial suspension was cultured overnight (15 h) in a thermostatic shaker at 37 °C and 200 rpm.

**(3) Sample preparation**

The samples were placed into sterile disposable culture dishes according to the experimental groups and sterilized under UV irradiation for 30 min before use.

For the covering film treatment, the covering film was cut into circular pieces with a diameter of 3 cm, immersed in ethanol for 1 h, and then air-dried before use.

**(4) Co-culture and plate-counting antibacterial test**

The *Staphylococcus aureus* suspension was diluted to $10^5$ CFU/mL using the 1/500 NB aqueous solution. Subsequently, 150 μL of the diluted bacterial suspension was evenly dropped onto the surface of each sample. A sterilized covering film was carefully placed onto the sample surface using sterile tweezers to ensure uniform contact between the bacteria and the sample surface, while preventing the bacterial suspension from overflowing beyond the edge of the covering film. The samples were then incubated statically at 37 °C for 24 h. After incubation, the bacteria were eluted using 1.5 mL sterile PBS solution. The recovered bacterial suspension was serially diluted by a factor of 10, and 100 μL of each diluted suspension was evenly spread onto LB solid medium plates. The plates were incubated at 37 °C for 3, 12, and 24 h, followed by colony counting. The colony-counting principle, bacterial concentration calculation method (CFU/mL), and antibacterial-rate calculation were the same as those described for the antibacterial evaluation against *E. coli* in Section S10.1.

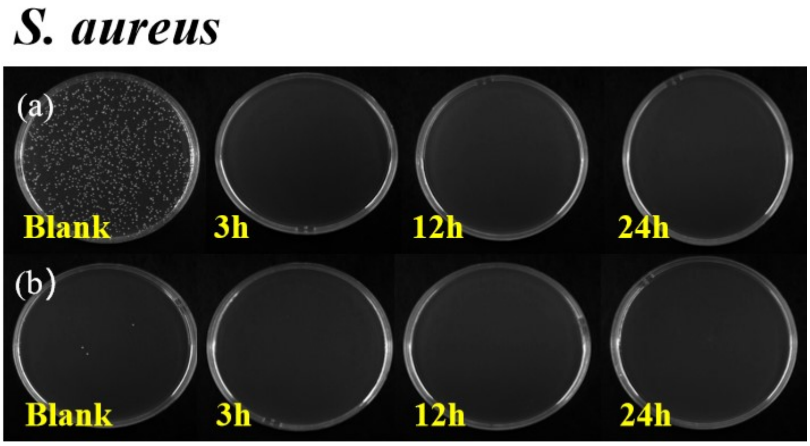

**Fig.S10** Antibacterial effect of $(12I\text{-}TA)_8T_2$ (a) and $(12I\text{-}TA)_7T_3$ (b) against *S.aureus* in 3, 12, and 24 h, with the blank group as control.

**Table S14** Antibacterial performance of $(12I\text{-}TA)_mT_n$ resins against *S aureus* after 24 h

| Group | Colony count | Dilution factor | Bacterial concentration (CFU/mL) | Antibacterial rate |
|---|---|---|---|---|
| Blank | 120 | $10^3$ | $2.60\times10^7$ | |
| $(12I\text{-}TA)_8T_2$ | 0 | $10^1$ | ＜$1.00\times10^3$ | ＞99.92% |
| $(12I\text{-}TA)_7T_3$ | 0 | $10^1$ | ＜$1.00\times10^3$ | ＞99.92% |
| $(12I\text{-}TA)_6T_4$ | 0 | $10^1$ | ＜$1.00\times10^3$ | ＞99.92% |

## S11. LDH cytocompatibility evaluation

L929 mouse fibroblast cells were cultured in complete medium consisting of low-glucose DMEM supplemented with 10% fetal bovine serum and 1% penicillin–streptomycin under a humidified atmosphere containing 5% $CO_2$ at 37 °C. When the cell confluence reached approximately 80%, the cells were detached using 0.25% trypsin-EDTA and used for subsequent experiments.

For the indirect extract-contact assay, photocured resin samples were prepared as circular disks (diameter: 10 mm). The samples were sterilized by immersion in 75% ethanol for 15 min, rinsed with sterile PBS, air-dried, and further sterilized under UV irradiation for 15 min on each side. Subsequently, each sample was immersed in 500 μL complete culture medium in a 48-well plate and incubated at 37 °C for 24 h to obtain the 100% extract medium. The extract was further diluted with fresh culture medium to obtain 75%, 50%, and 25% extract concentrations. Culture medium incubated under identical conditions without resin samples was used as the control group.

LDH release was evaluated using an LDH cytotoxicity assay kit according to the manufacturer’s instructions. L929 cells were seeded into 96-well plates and incubated with the resin extracts for 24 h. The culture supernatants were collected to determine spontaneous LDH release. To determine the maximum LDH release, the corresponding cells were lysed using the supplied lysis buffer. Subsequently, 100 μL LDH working solution was added to each collected supernatant and lysate, followed by incubation at room temperature for 25 min in the dark. The absorbance was measured at 450 nm with a reference wavelength of 650 nm.

In addition, direct-contact LDH assays were also conducted to further evaluate the short-term cytocompatibility of the photocured resin. The results are shown in Fig.S10 and Fig.S11. All quantitative data were expressed as mean ± standard deviation (SD) from four independent experiments (n = 4). Statistical analyses were performed using one-way ANOVA followed by Dunnett’s multiple comparison test and Tukey’s post hoc test. Statistical significance was defined as *P < 0.05, **P < 0.01, and ***P < 0.001.

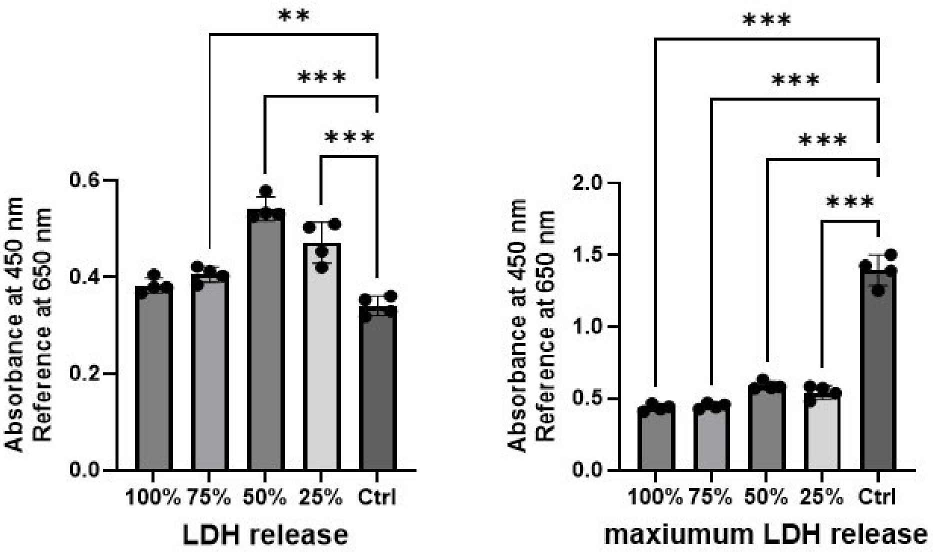

**Fig.S11** LDH release and maximum LDH release of L929 cells cultured with different concentrations of $(12I\text{-}TA)_6T_4$ resin extracts for 24 h.

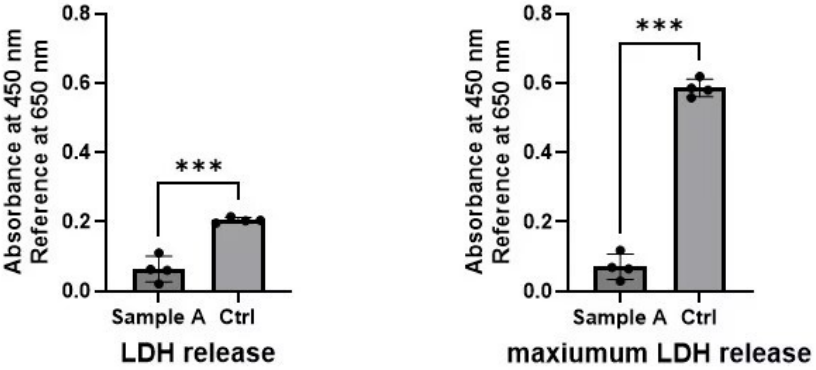

**Fig.S12** Direct-contact LDH release and maximum LDH release of L929 cells after incubation with the photocured $(12I\text{-}TA)_6T_4$ resin for 24 h.