Supplementary Information (SI) for Green Chemistry.
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Supporting Information:

Fully Bio-Based Cellulose Vitrimers with Dynamic Enamine Bonds: Toward Recyclable and Micropatternable Green Materials

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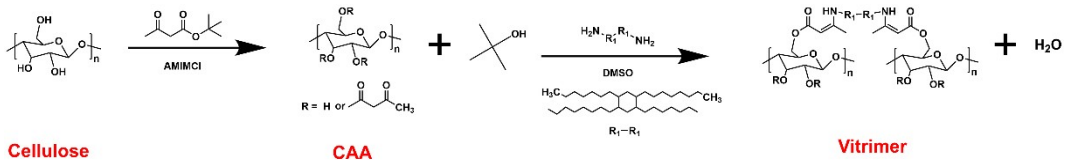

Figure S1. A detailed reaction scheme with explicit annotation of by-products (tert-butanol and water).

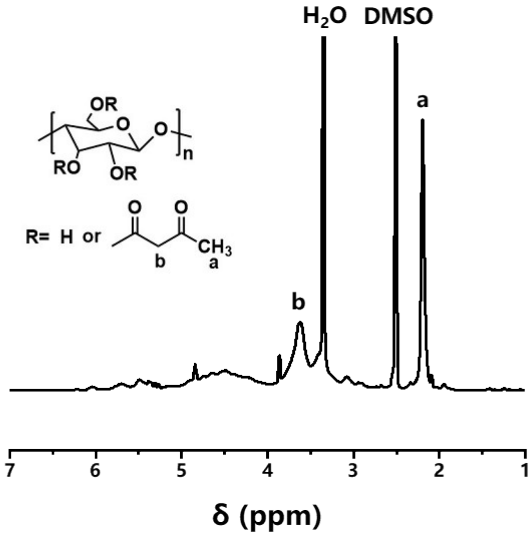

Figure S2. ^{1}H-NMR spectrum of CAA in DMSO-d6.

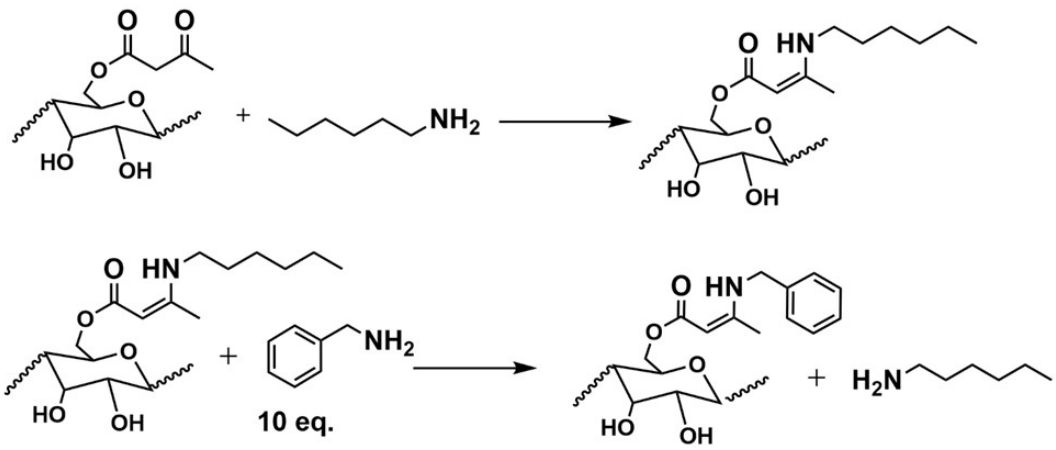

Figure S3. Chemical structural formula of the model reaction.

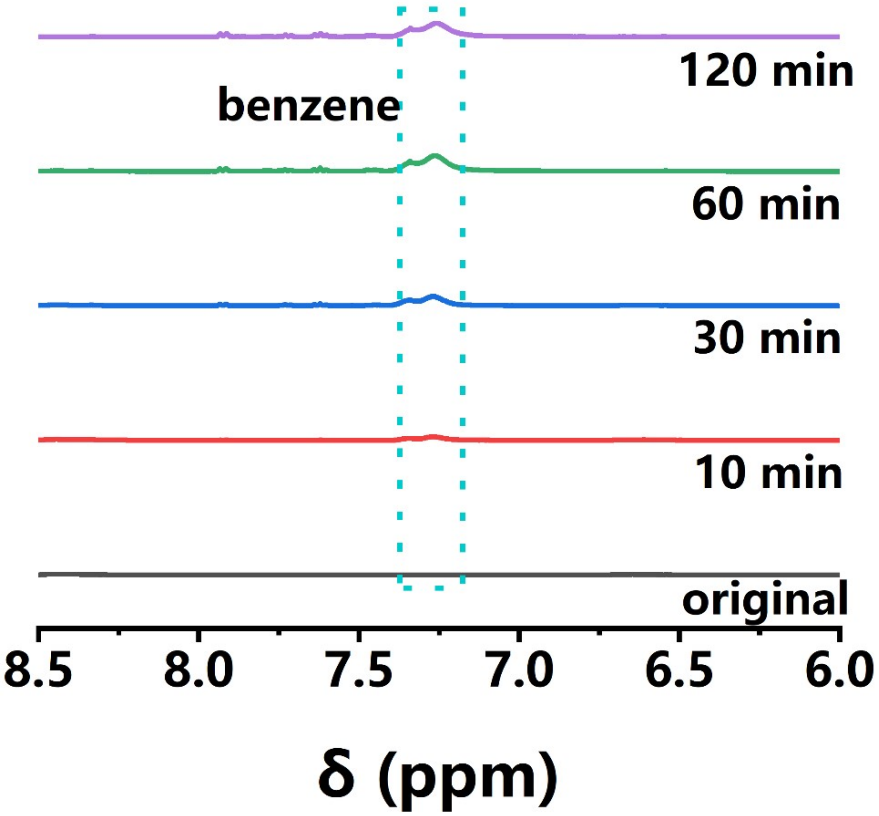

Figure S4. ^{1}H-NMR spectra tracing the model reaction.

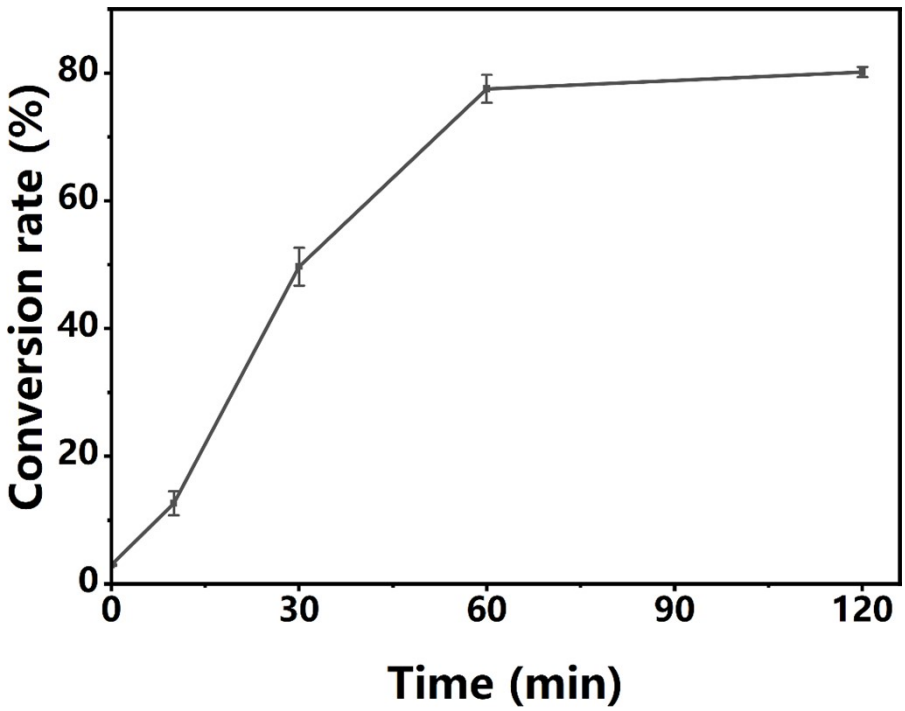

Figure S5. Reaction conversion rate of the model reaction.

Table S1. Degree of polymerization of different cellulose raw materials.

Raw materials	Degree of polymerization
Microcrystalline cellulose	221
Wood pulp	856
cotton	1925

[a] The author conducted experiments in the laboratory using the copper-ammonia method to determine the cellulose polymerization degree.

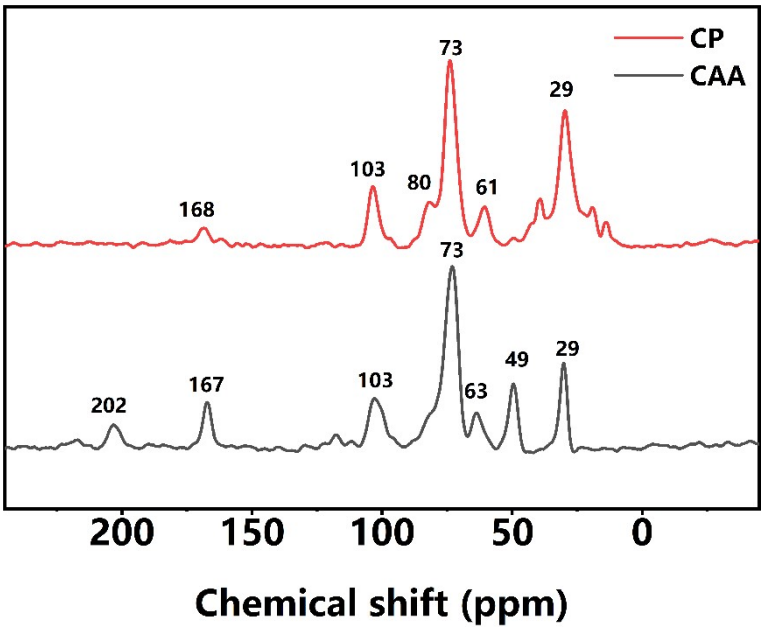

Figure S6. Solid-state ^{13}C NMR spectra of CAA and CP vitrimer.

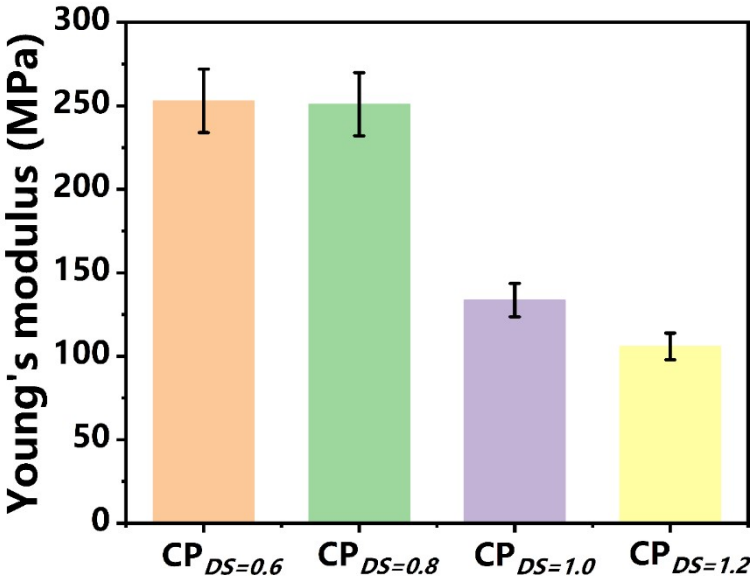

Figure S7. Young's modulus of bio-based vitrimers ($CP_{DS=0.6}$, $CP_{DS=0.8}$, $CP_{DS=1.0}$, $CP_{DS=1.2}$).

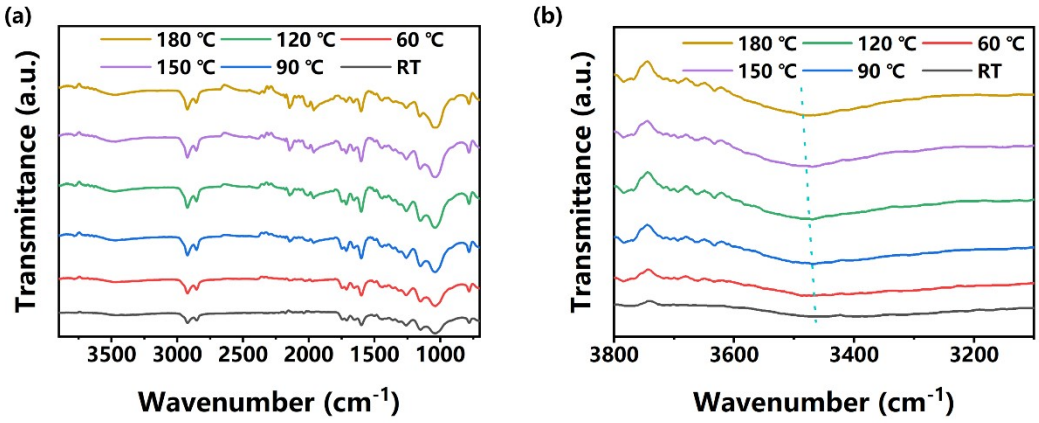

Figure S8. FTIR spectra of CP in different temperature(a) Full Scope (b) Partial Scope.

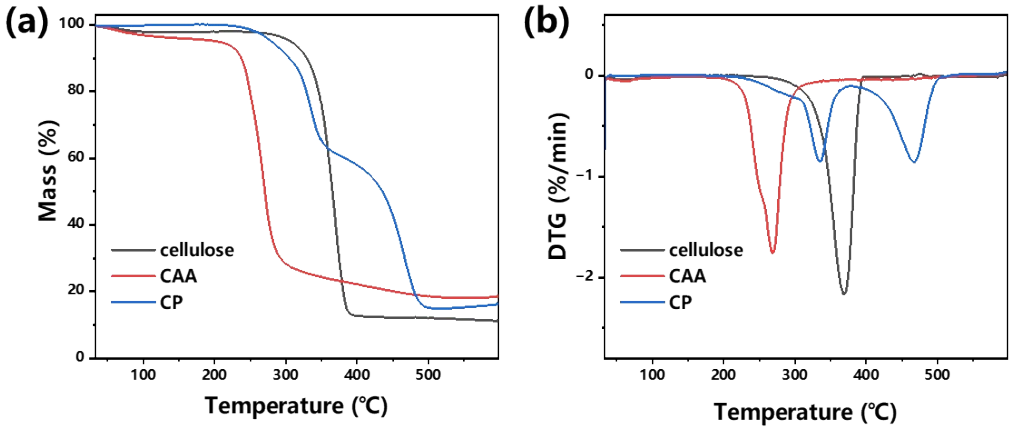

Figure S9. TG (a) and DTG (b) curves for CP, CAA, cellulose.

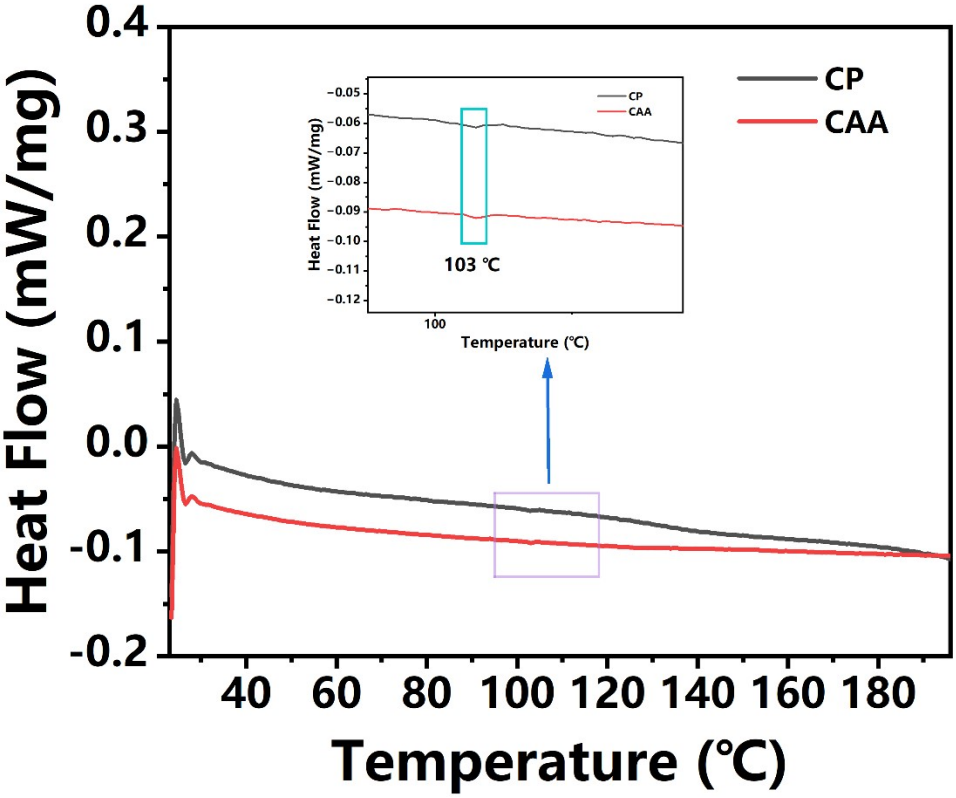

Figure S10. DSC curves for CP, CAA.

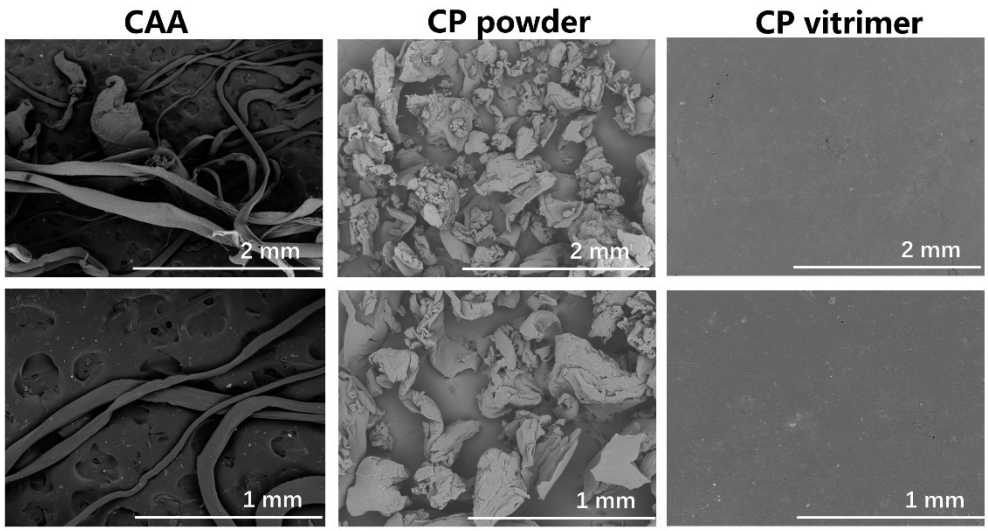

Figure S11. The SEM images of CAA, CP powder and CP vitrimer surfaces.

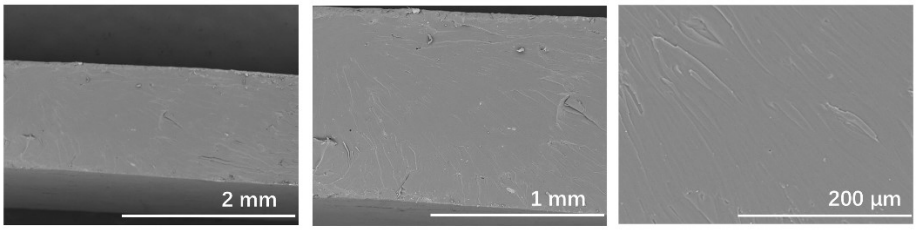

Figure S12. The SEM images of the CP cross-section.

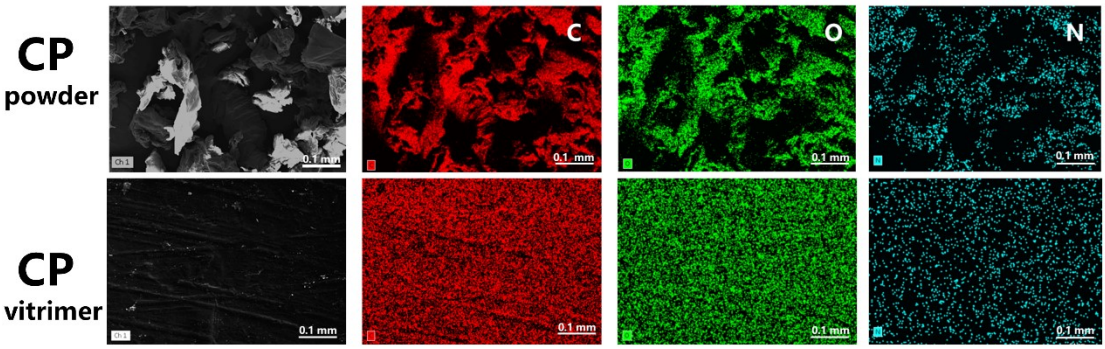

Figure S13. The EDS mapping images of the CP powder and CP vitrimer.

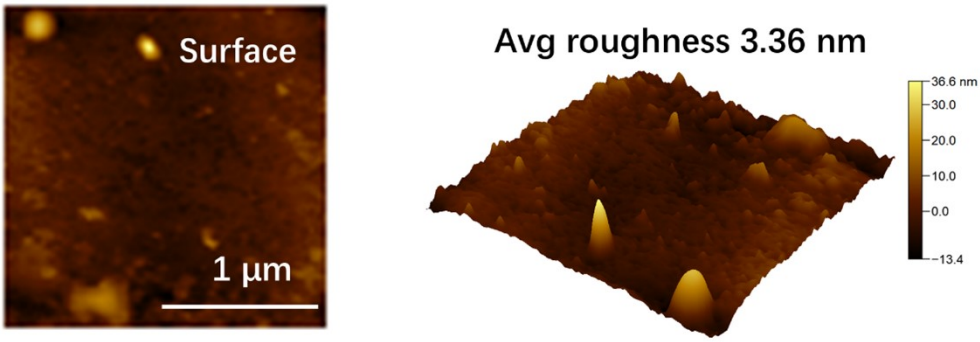

Figure S14. The AFM images of the CP surface.

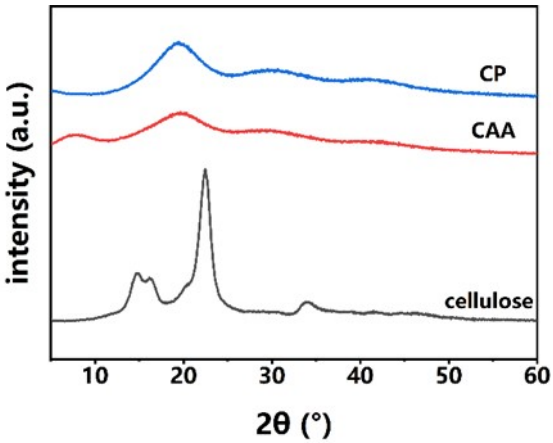

Figure S15. XRD images of cellulose, CAA and CP.

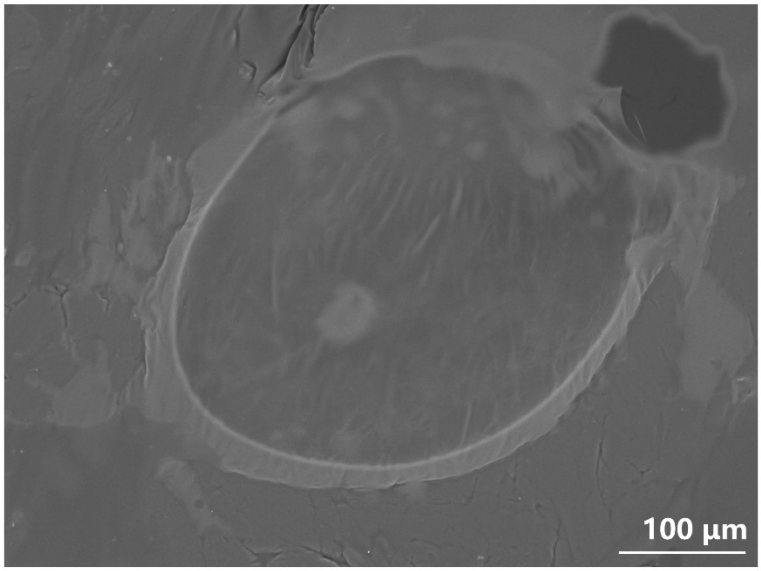

Figure S16. The SEM image of the etching area in the CP.

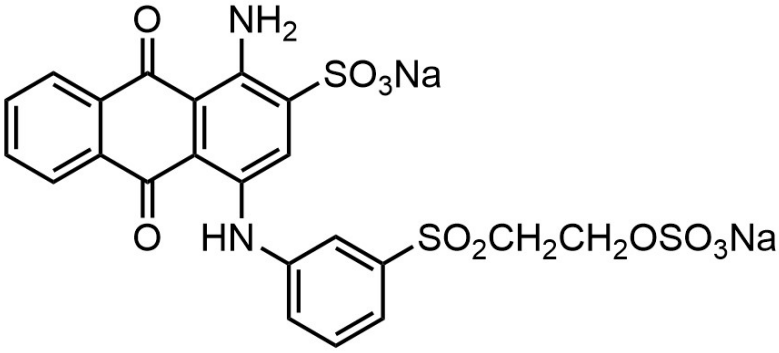

Figure S17. The structural formula of the dye.

Green chemistry metrics

The system's green chemistry profile was assessed using the following parameters:

(a) Atom economy (AE)

AE quantifies the efficiency of a chemical reaction and is defined as the percentage of atoms from the reactants that are incorporated into the desired product[1, 2]. The ideal AE value of 100% signifies complete atom retention from the starting materials. For the CAA and CP samples, AE values were determined via Equation S1:

$$AE\ (\%) = \frac{Molecular\ weight\ of\ the\ product}{\sum Molecular\ weight\ of\ reactants} \times 100 \qquad \text{(S1)}$$

(b) Environmental factor (E-factor) and process mass intensity (PMI) analysis

According to established definition[3, 4], the E-factor evaluates the sustainability of a chemical process by quantifying the mass of waste generated per unit of product. Assuming complete ethanol recovery, the E-factor values for the CP samples were obtained from Equation S2:

:

$$E-factor = \frac{\sum m(raw\ materials) + \sum m(spent\ reagents) + \sum m(solvent\ losses) - m}{m(product)} \qquad \text{(S2)}$$

As a key efficiency metric, PMI accounts for the total mass of all materials used divided by the mass of the obtained product. The corresponding PMI values for CP were evaluated via Equation S3:

$$PMI = \frac{\sum m(raw\ materials) + \sum m(reagents) + \sum m(solvent)}{m(product)} \qquad \text{(S3)}$$

(c) Biorenewable carbon (BRC) content

BRC content represents the fraction of total carbon originating from renewable biomass sources[5]. For the CP samples, BRC values were evaluated via equation S4:

$$BRC\ (\%) = \frac{Biosourced\ carbon}{Biosourced\ carbon\ +\ Fossil\ carbon} \times\ 100 \tag{S4}$$

(d) Energy consumption

The energy consumption across individual processing steps was evaluated using the rated power of the laboratory equipment and its respective runtime[6], following Equation S5:

$$E\ =\ \sum(Pi\ \times\ ti) \tag{S5}$$

where E represents the total energy consumption, Pi is the rated power of each laboratory device, and ti is its corresponding operational time. The reported values are laboratory-scale estimates derived from a representative batch that started with 8 g of cellulose as the raw material.

Table S2. Detailed material quantities and derived carbon for each synthetic step.

Step	Material	Type	Output	MW (g/mol)	Equiv.	Mol	Weight (g)	Derived carbon (after calculation)
	Cotton	Raw material		162.1	1.0	0.05	8.1	6
	AMIMCl	Solvent		158.6			151.9	
1	DMF	Reagent		73.1			80.0	
	t-BAA	Raw material		158.2		0.46	73.2	3.2
			CAA	230.1			9.2	
	CAA	Intermediate		230.1	1.0	0.05	9.2	
	DMSO [a]	Solvent		78.1			80	
2	Priamine 1075	Raw material		530	Acetoacetate/ amine=1：1.1	0.03	14.6	15.8
			CP	448.6			17.9	25

The material inputs were estimated based on a representative CP preparation batch.

For the above data, the contribution values were calculated as DS × M, where DS = 0.8.

a DMSO could be removed by rotary evaporation.

Table S3. Material efficiency metrics.

Step	Sample	AE (%) [a]	E-factor	PMI (g/g)	BRC%
1	CAA	71.8	33.0 [b]	34.0	65.2
2	CP	95.9	0.3	5.8	87.2

For the above data, the contribution values were calculated as DS × M, where DS = 0.8.

a The molecular weight of the reactant used in Step 1 was 320.3 g/mol, and that used in Step 2 was 463.3 g/mol.

b The E-factor could be reduced even further through the use of spray drying.

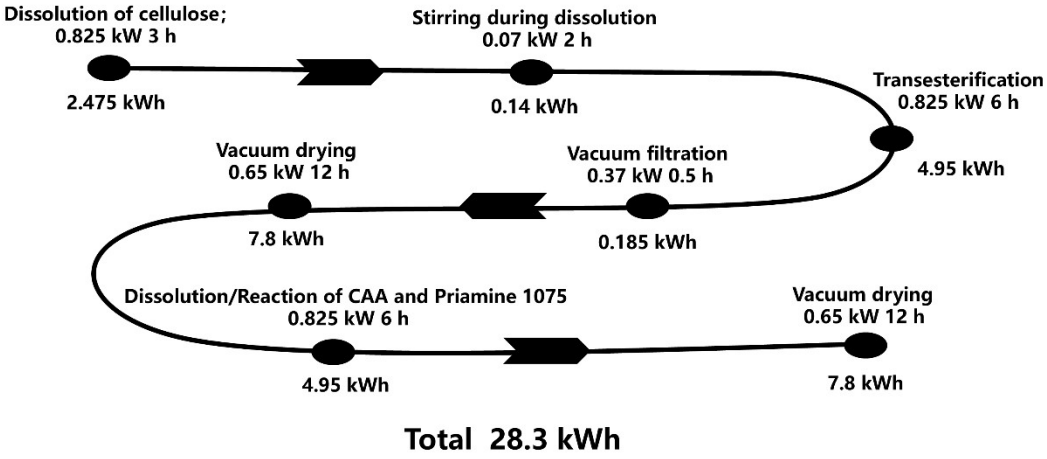

Figure S18. Flowchart of the experimental energy consumption calculation (Laboratory-scale).

Table S4 The green advance of this work compared with the previous literatures

Raw material	Crosslinking conditions		Hot pressing conditions				Degradation time (efficiency)	Reference
	Temperature (℃)	Time (h)	Temperature (℃)	Time (h)	Pressure	Catalyst		
Cellulose acetoacetate/Priamine 1075 (Plant oil)	**25-100**	**2-6**	**120**	**0.25**	**30 MPa (6.2 kN)**	**No**	**56 d (90%)**	**This work**
Epoxy dicardanol-based succinate	80-150	2	160-180	1	20 MPa	1, 5, 7-triazadicyclic [4.4.0] deca-5-ene	No data	[7]
Cardanol-based vinylogous urethane vitrimer	130	About 3	130	1	10 MPa	No	No data	[8]
Cardanol-based epoxy novolac resin/Itaconic acid	120-150	2	180	1	130 kN	2-ethyl-4-methylimidazole and zinc triflate Zinc salt	No data	[9]
Chitosan/Vanillin	80	9	130	0.5	20 MPa	No	100 d (70%)	[10]
Softwood kraft lignin/ poly(ethyleneglycol)divinyl ether	110	6	150	12	0	No	No data	[11]

Starch-reinforced vinylogous urethane vitrimer composites	135	0.75	160	0.18	10 MPa	No	No data	[12]

Reference:

(1) Sheldon, R. A. The e factor: Fifteen years on. *Green Chemistry* **2007**, *9* (12), 1261-1384. DOI: 10.1039/b713736m.

(2) Chen, Y.; Xie, C.; Wu, T.; He, T.; Xie, H.; Guo, Y. Water-mediated fabrication of reprocessable and self-healing cellulose-based polyimine plastics. *Green Chemistry* **2026**. DOI: 10.1039/d6gc01654e.

(3) Sheldon, R. A. E factors, green chemistry and catalysis: An odyssey. *Chemical Communications* **2008**, (29). DOI: 10.1039/b803584a.

(4) Sheldon, R. A. The e factor 25 years on: The rise of green chemistry and sustainability. *Green Chemistry* **2017**, *19* (1), 18-43. DOI: 10.1039/c6gc02157c.

(5) Skliutas, E.; Lebedevaite, M.; Kasetaite, S.; Rekštytė, S.; Lileikis, S.; Ostrauskaite, J.; Malinauskas, M. A bio-based resin for a multi-scale optical 3d printing. *Scientific Reports* **2020**, *10* (1). DOI: 10.1038/s41598-020-66618-1.

(6) Cespi, D. Procedural life cycle inventory of chemical products at laboratory and pilot scale: A compendium. *Green Chemistry* **2024**, *26* (18), 9554-9568. DOI: 10.1039/d4gc01372g.

(7) Hu, Y.; Tong, S.; Hu, L.; Zhang, M.; Huang, Q.; Sha, Y.; Jia, P.; Zhou, Y. Molecularly engineered cardanol derived epoxy vitrimers based on dynamic disulfide and dynamic ester exchanges with desirable dynamic response, degradability, and recyclability. *Chemical Engineering Journal* **2023**, *477*, 147284. DOI: 10.1016/j.cej.2023.147284.

(8) Chen, F.; Gao, F.; Zhong, J.; Shen, L.; Lin, Y. Fusion of biobased vinylogous urethane vitrimers with distinct mechanical properties. *Materials Chemistry Frontiers* **2020**, *4* (9), 2723-2730. DOI: 10.1039/d0qm00302f.

(9) Albertini, E.; Dalle Vacche, S.; Bongiovanni, R.; Bianco, I.; Blengini, G. A.; Vitale, A. Biobased and reprocessable vitrimers based on cardanol-derived epoxy for more sustainable thermosets. *ACS Sustainable Chemistry & Engineering* **2025**, *13* (5), 2120-2131. DOI: 10.1021/acssuschemeng.4c09035.

(10) Zhang, X.; Lin, L.; Zhou, H.; Zhou, G.; Wang, X. All-natural chitosan-based polyimine vitrimer with multiple advantages: A novel strategy to solve nondegradable plastic waste pollution. *Journal of Hazardous Materials* **2024**, *465*, 133030. DOI: 10.1016/j.jhazmat.2023.133030.

(11) Moreno, A.; Morsali, M.; Sipponen, M. H. Catalyst-free synthesis of lignin vitrimers with tunable mechanical properties: Circular polymers and recoverable adhesives. *ACS Applied Materials & Interfaces* **2021**, *13* (48), 57952-57961. DOI: 10.1021/acsami.1c17412.

(12) Haida, P.; Chirachanchai, S.; Abetz, V. Starch-reinforced vinylogous urethane vitrimer composites: An approach to biobased, reprocessable, and biodegradable materials. *ACS Sustainable Chemistry & Engineering* **2023**, *11* (22), 8350-8361. DOI: 10.1021/acssuschemeng.3c01340.