Supporting information:

One-pot cellulose etherification and self-crosslinking via mild hydroxyl-yne click reaction in homogeneous system

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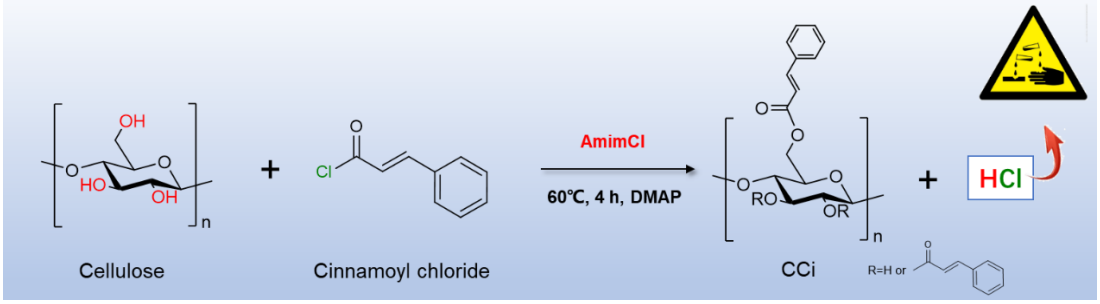
Preparation of cellulose cinnamate

From the similarity of the chemical structure, cellulose cinnamate (CCi) containing alkene bonds, unsaturated bonds and benzene rings, was also prepared. The viscosity of the reaction mixture and the solubility of CCi were further investigated. Cellulose cinnamate was synthesized by the acylation of cellulose under AmimCl homogeneous condition using DMAP as catalyst. The dried cellulose was added to a certain amount of AmimCl (5 g) and 3mL DMF, and heated in oil bath for 30 min at 80 °C with mechanical stirring. The clear and viscous cellulose/ solution obtained was allowed to cool to room temperature. 0.1028 g (0.617 mmol) of cinnamate chloride and 0.075 g (0.0617 mmol) of DMAP were added to clear and viscous cellulose (0.1 g, 0.617 mmol) /AmimCl solution. The mixture was stirring for 4 h under 60 °C and subsequently precipitated in 200 ml of methanol. The pure product of CCi was dried in vacuum.



Scheme S1 Synthesis of cellulose cinnamate (CCi)

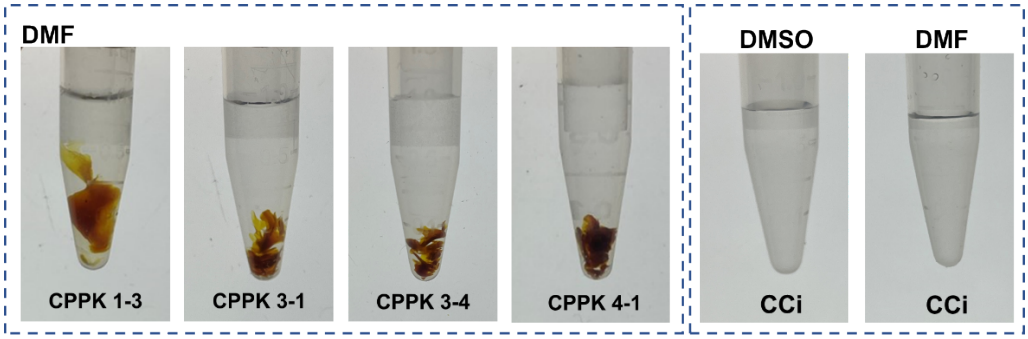


Figure S1. Solubility of the CPPKs and CCi sample

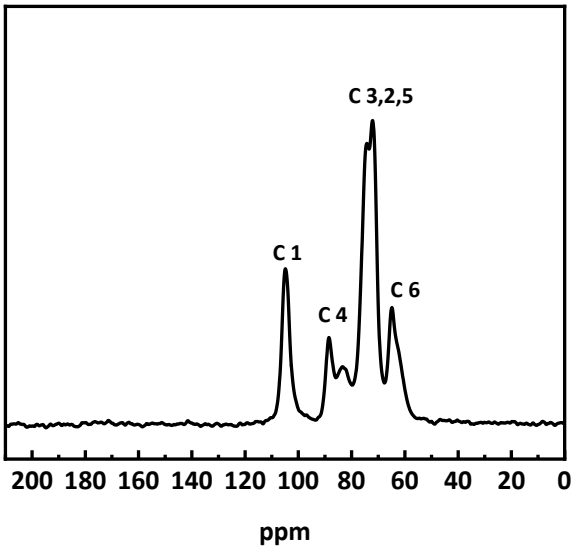


Figure S2. ^{13}C NMR spectra of cellulose

The XRD of cellulose, regenerated cellulose (re-cellulose) and CPPK3-1

The change in the crystalline structure of cellulose during dissolution and click reaction was studies using X-ray diffraction (XRD). The native crystalline structure of cellulose is cellulose I. Obviously, a typical pattern of Cellulose I was observed for raw cellulose with the main peaks at 14.7°, 16.4°, 20.6°, 22.7°, and 34.1°. In this work, after dissolution-modification-regeneration. cellulose I transforms into a more stable cellulose II phase (Re-cellulose and CPPK), as indicated by the typical diffraction peaks observed at 2θ = 12.1°, 20.0°, respective. (Figure S3).

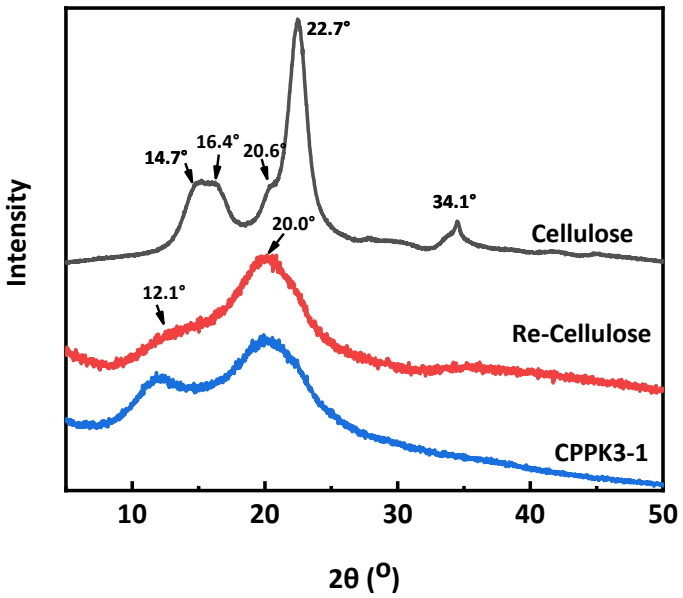


Figure S3. XRD patterns of cellulose, regenerated cellulose (re-cellulose) and CPPK3-1

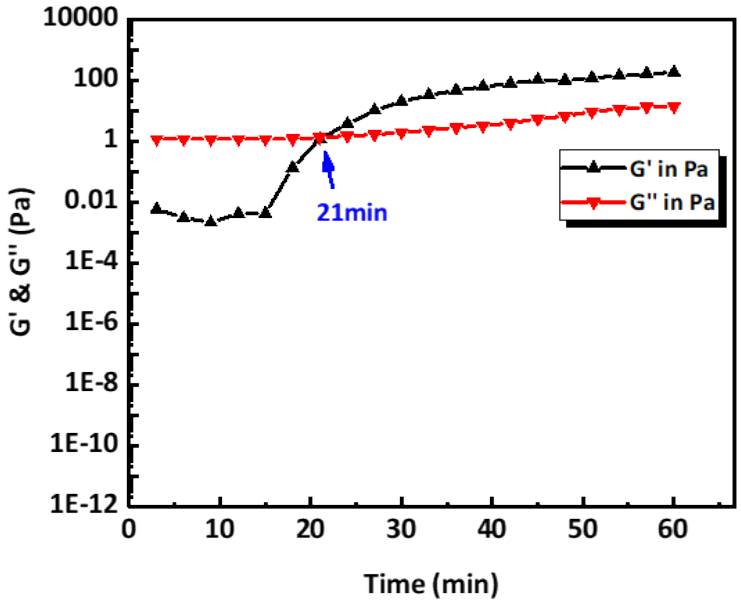


Figure S4. G’ and G” of the CPPK 1-3 solutions on time with a frequency of 1Hz

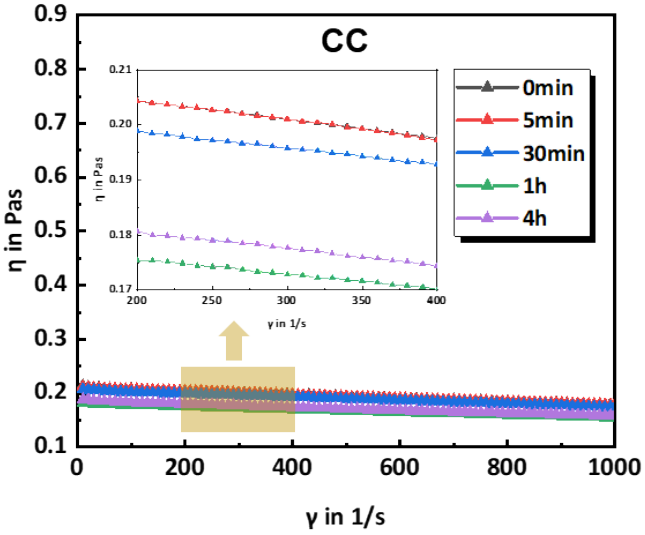


Figure S5. Viscosity of different reaction time of cellulose cinnamate (CC)

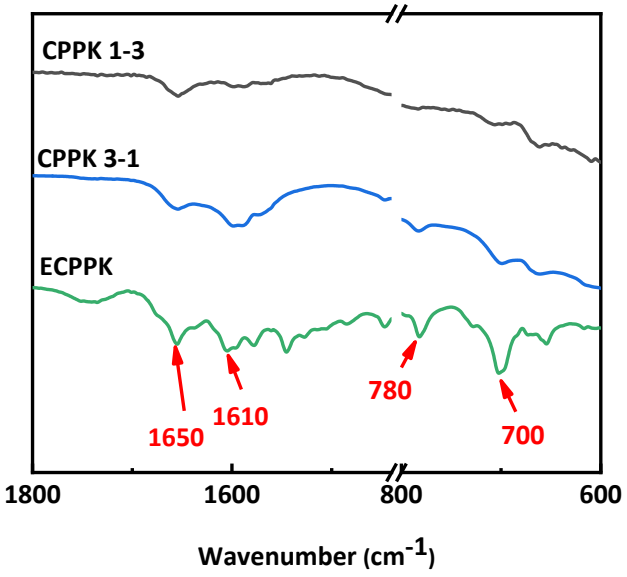


Figure S6. FTIR spectra of CPPK1-3, CPPK 3-1 and ECPPK

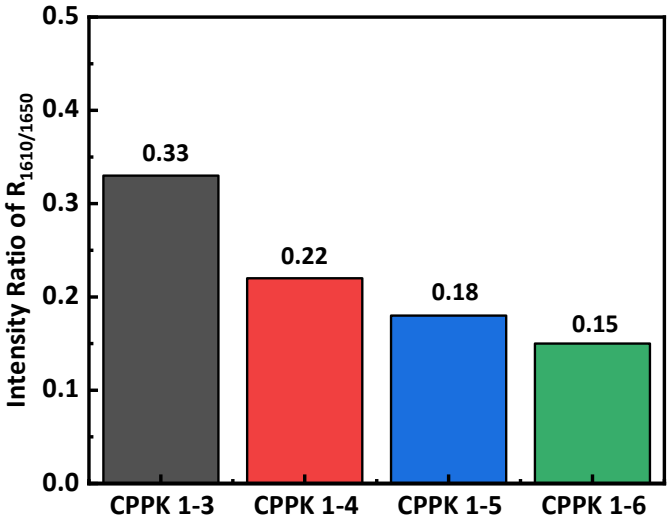


Figure S7. The intensity ratio of CPPK with different reaction temperature.

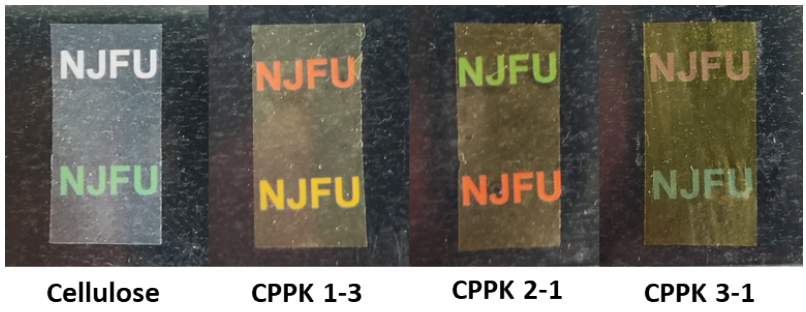


Figure S8. The photographs of films of cellulose and CPPKs

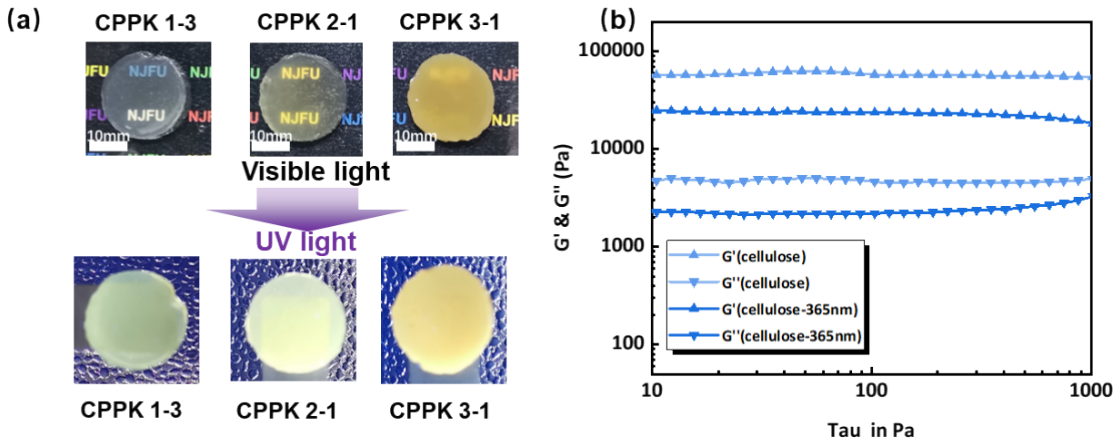


Figure S9. (a) The photographs of CPPK hydrogel before and after UV irradiation. (b) Viscoelastic diagram of cellulose hydrogel before and after UV irradiation.

Table S1. Comparison in the hydroxyl-yne click reaction applied in this work with other chemical reactions applied to cellulose materials.

Entry	Products	Derivatization reagents	Temperature (°C)	molar ratio of AGU/Derivatization reagents	Time	Byproducts	Stress (MPa)	Ref.
1	amino cellulose (AC)	ethanediamine	100	1:25	6 h	HCl	8.93	1
2	stearoylated and cinnamoylated cellulose esters (SCC)	stearoyl chloride cinnamoyl chloride	100	1:6.7	5 h	HCl	25	2
3	microcrystalline cellulose nitrilotriacetic acid esters (MCN)	nitrilotriacetic acid anhydride	75	1:0.66	12 h	-	58.46	3
4	cellulose acetate (CA)	acetic anhydride	110	1:5	2 h	-	59.5	4
5	3-pentadecylphenoxy acetic acid/acetic anhydride mixed cellulose esters (PA/Ac MCE)	3-pentadecylphenoxy acetic acid/acetic anhydride	100	1:6	6 h	-	84	5
6	aliphatic stearoyl/ acetic anhydride mixed cellulose esters (St/Ac MCE)	aliphatic stearoyl/ acetic anhydride	100	1:6	6 h	-	85	5
7	cellulose-lignin (CL)	lignin	50	-	12 h	-	90	6
8	cellulose cinnamate (CCi)	cinnamoyl chloride	60	1:2.33	3 h	HCl	92.4	7
9	stearoylated and cinnamoylated cellulose esters under UV irradiation (SCC-UV)	stearoyl chloride cinnamoyl chloride	100	1:6.7	5 h	HCl	60	2
10	crosslinked regenerated cellulose (CRC)	glutaric dialdehyde	60	-	20 min	-	76.8	8
11	anisotropic cellulose films (ACF)	epichlorohydrin	0	1:1.33	2 h	HCl	81.8	9
12	lauroylated and cinnamoylated cellulose esters under UV irradiation (LCC-UV)	lauroyl chloride cinnamoyl chloride	100	1:7.6	5 h	HCl	90	2
13	CPPK CPPK UV	PPK	25	1:2 1:1	4 h	-	85.7 ± 1.5 88.8 ± 1.7	This work

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