Supporting Information for

A novel DLP printing strategy of collagen-based bioink with prospective crosslinker procyanidins

Zilin Wu, Jing Liu, Jianjun Lin, Lu Lu, Jihuan Tian, Lihua Li *, Changren Zhou*

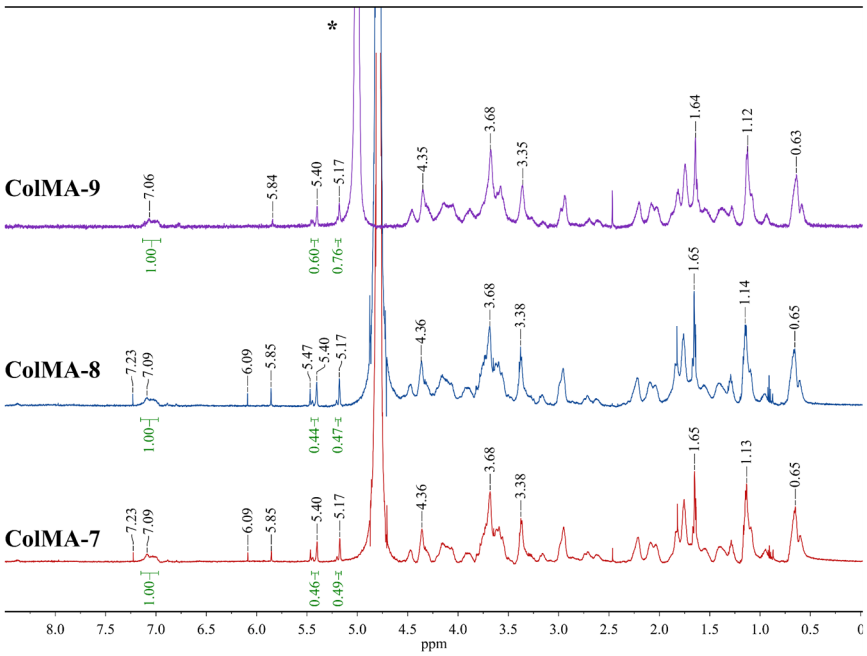

Figure S1. ^{1}H NMR spectra of ColMA-7, ColMA-8 and ColMA-9 recorded in 1% DCl D_2O (*). The peaks at 7.09 ppm from the aromatic residues of collagen and the peaks at 5.40 ppm and 5.17 ppm from the olefinic protons of methacrylate groups was integrated to estimate the degree of substitution.

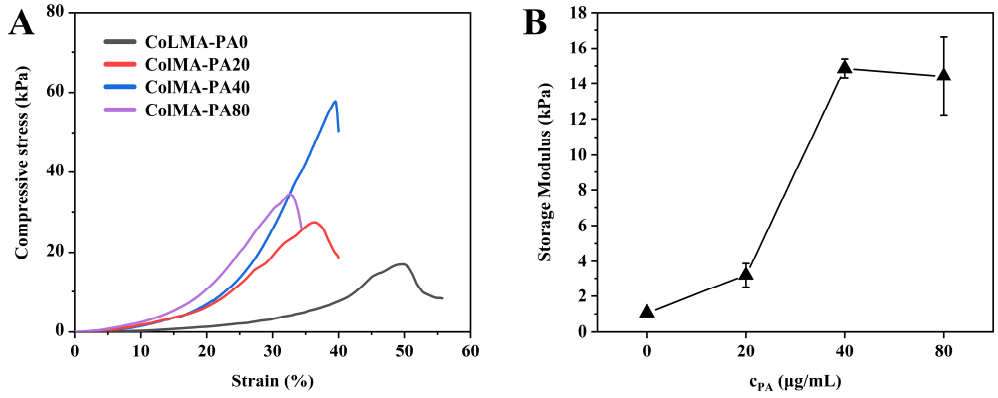

Figure S2. (A) Compression test results of ColMA-PA hydrogels. (B) Storage modulus of ColMA bioinks with different PA concentrations.

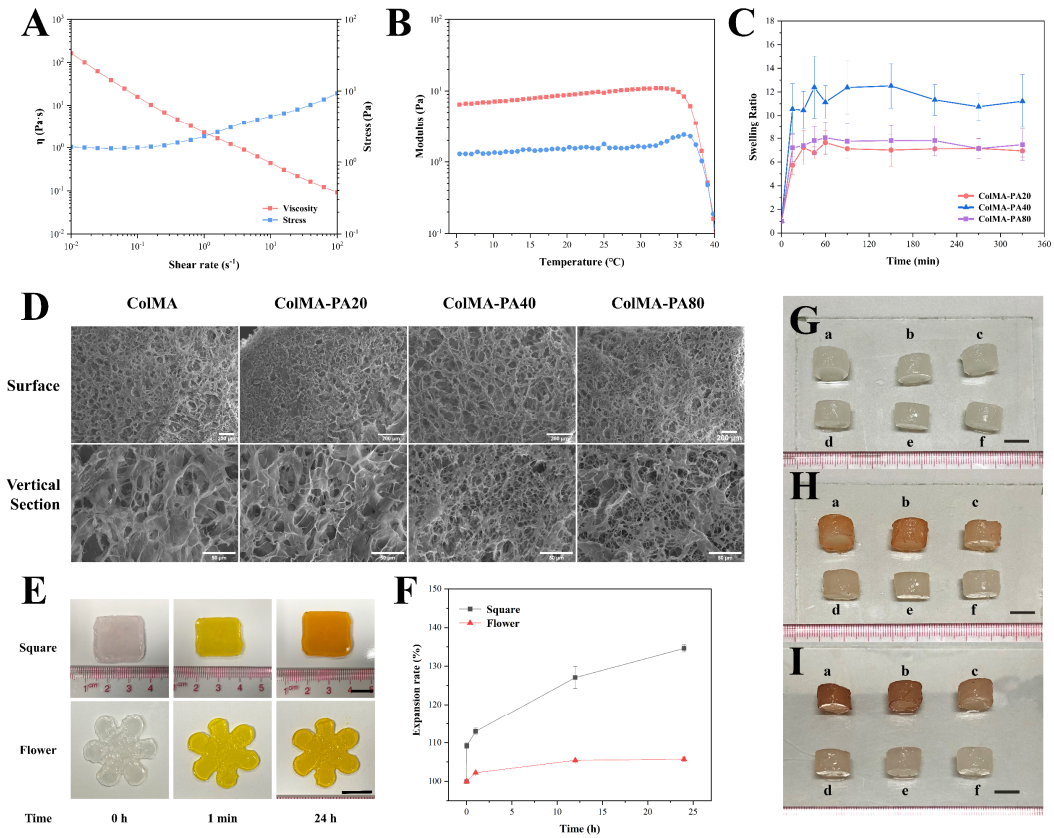

Figure S3. (A) Flow curves of ColMA-PA40 bioink. (B) Temperature sweep of ColMA-PA40 bioink. G', storage modulus; G'', loss modulus. (C) Microstructure of lyophilized ColMA hydrogels. (E-F) Expansion rate of ColMA-PA hydrogels. Scale bar indicates 1 cm. (G-I) Photographs of pristine ColMA hydrogels before (G) and after 15 h (H) and 24 h (I) incubation in PA solution. The concentrations of PA are (a) 320 μg/mL; (b) 160 μg/mL; (c) 80 μg/mL; d) 40 μg/mL; e) 20 μg/mL f) 0 μg/mL. Scale bar indicates 1 cm.

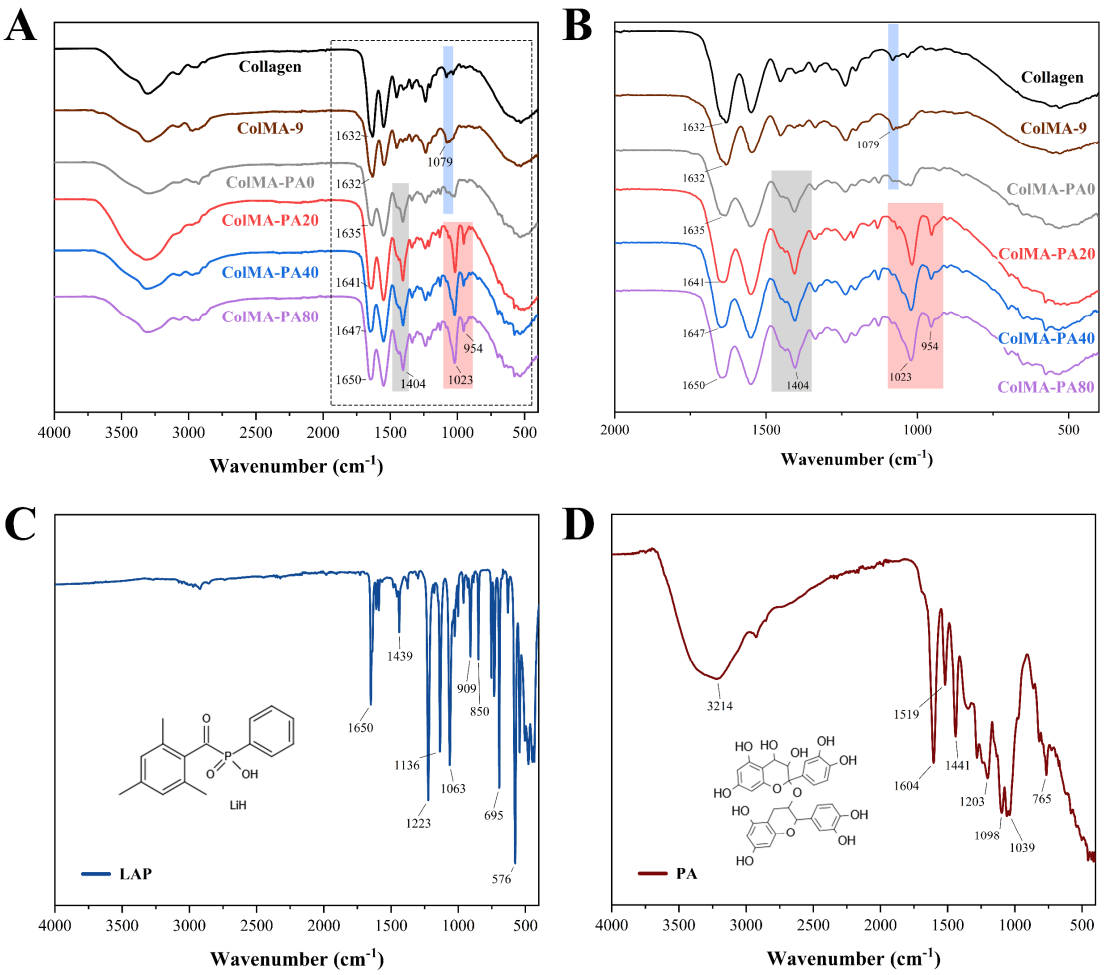

Figure S4. (A) FT-IR spectra of collagen, ColMA, and ColMA-PA lyophilized hydrogels. ColMA-9 represents the ColMA prepared at pH 9. ColMA-PA0, ColMA-PA20, ColMA-PA40 and ColMA-PA80 represent the lyophilized ColMA-PA hydrogels with different PA concentrations. (B) An enlarged view of the wavenumber ranges from 2000 to 400 cm^{-1} in Figure S3A. (C) FT-IR spectrum of LAP (lithium phenyl-2,4,6-trimethylbenzoyl-phosphinate). (D) FT-IR spectrum of PA (procyanidins).

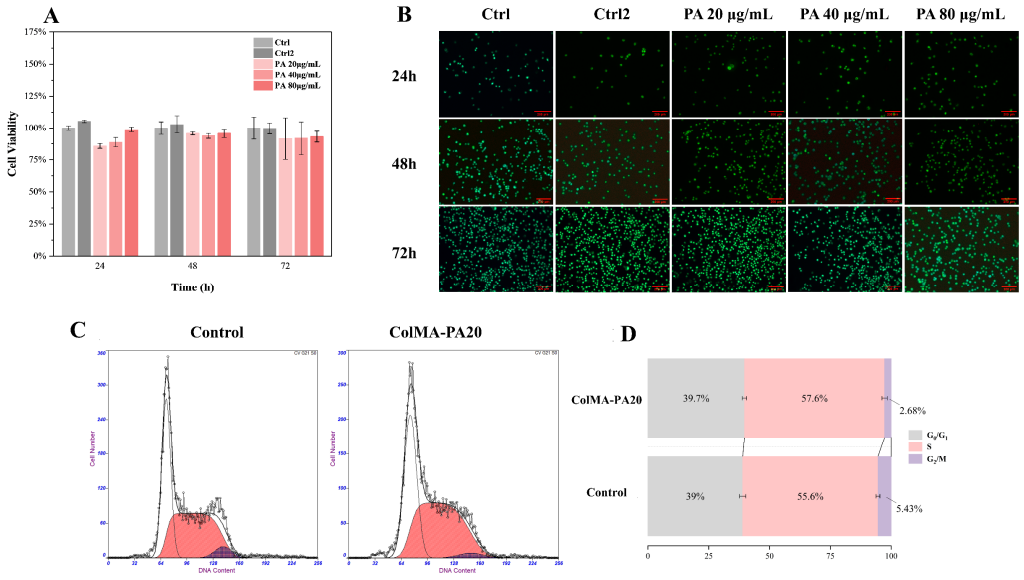

Figure S5. In vitro cytocompatibility of PA and ColMA-PA. (A) CCK-8 assay; the viability of L-929 cells cultured in different concentrations of PA for 3 days. (B) Live and dead assay of L-929 cells cultured in different concentrations of PA for 3 days. Live cells in green and dead cells in red. Scale bar indicates 200 μm. Ctrl group was given medium without DMSO and PA, and Ctrl2 group was given medium containing 0.1% DMSO to eliminate solvent interference. (C) Cell cycle histograms for the L-929 cells on culture plates (control group) and in the ColMA-PA20 hydrogels after 4 days of culture. (D) The population distribution for the cells on culture plates (control group) and in the ColMA-PA20 hydrogels after 4 days of culture.

Table S1. Swelling ratio and equilibrium water content of ColMA-PA hydrogels.

Hydrogel	ColMA-PA20	ColMA-PA40	ColMA-PA 80
Swelling ratio	7.33±0.45	11.48±1.48	7.63±0.82
Equilibrium water content	96.28±0.36%	96.76±0.05%	96.81±0.10%

Table S2. Compressive properties of ColMA-PA hydrogels

Hydrogel	ColMA	ColMA-PA20	ColMA-PA40	ColMA-PA80
Compressive stress at break (kPa)	15.84 ± 2.14	26.50 ± 2.33	49.62 ± 8.16	35.00 ± 3.71
Compressive strain at break (%)	48.85 ± 1.47	35.17 ± 3.96	36.9 ± 5.27	40.79 ± 7.19

Movie S1. The macroscopic liquidity and UV curing performance of ColMA-PA20 bioink. The 10 watts UV lamp at a wavelength of 365 nm has been used.

Movie S2. Three-dimensional distribution of L-929 cells in ColMA-PA20 hydrogel scaffold. The cytoskeletal actin fibers were stained with phalloidin (red) and the nuclei were stained with DAPI (blue).