

## Supporting Information

### **Facile synthesis of zinc chloride/formic acid based deep eutectic solvents for mild and efficient dissolution of collagen with high concentration**

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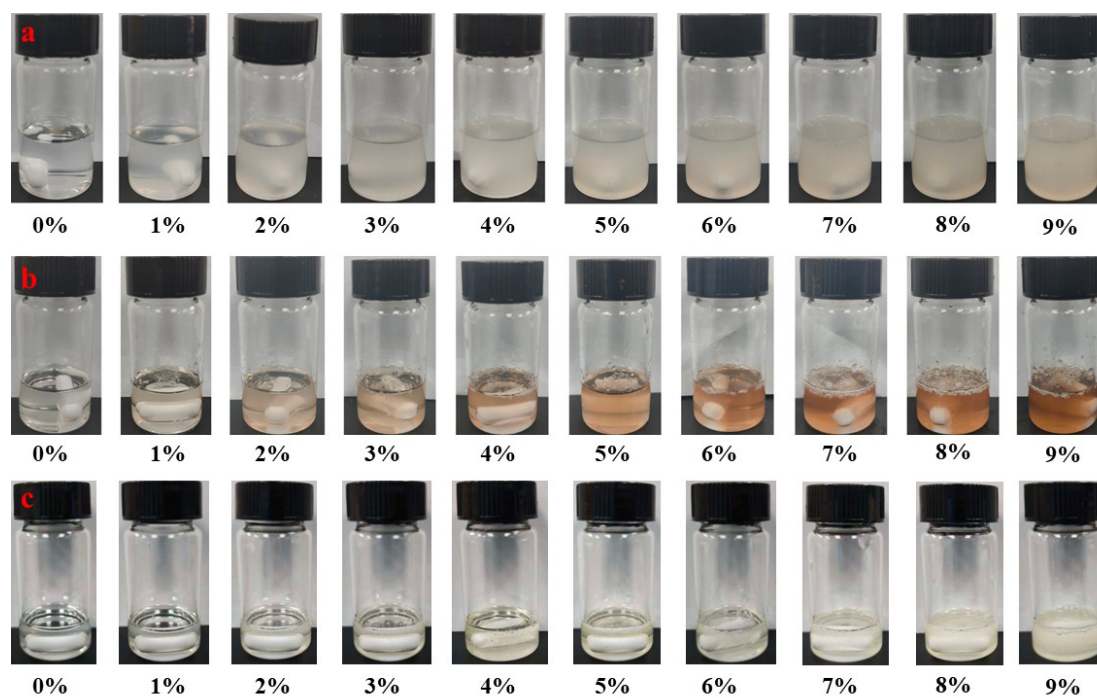
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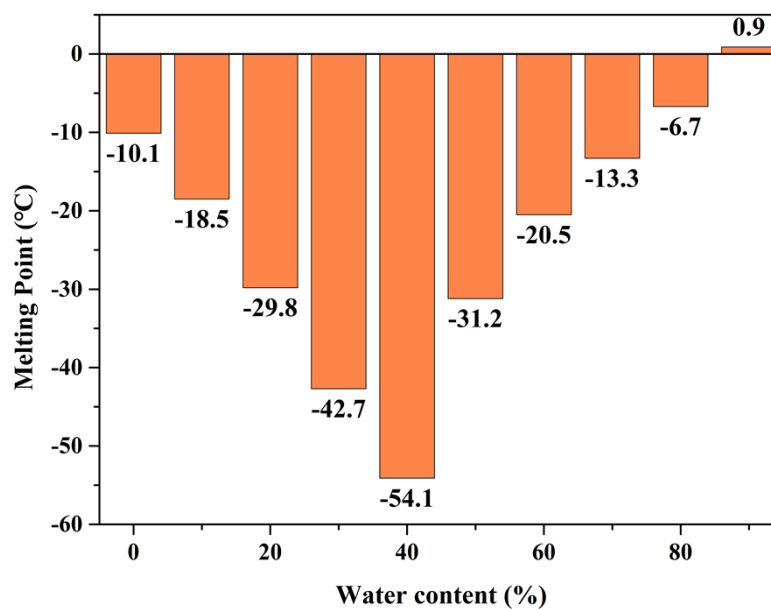
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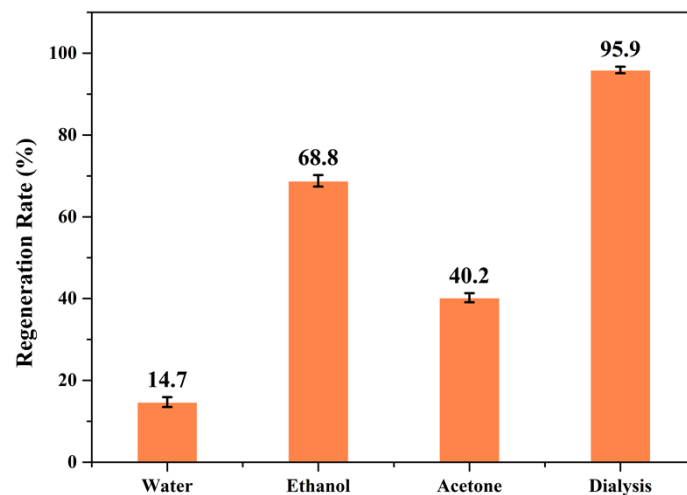
Table S1 to S7



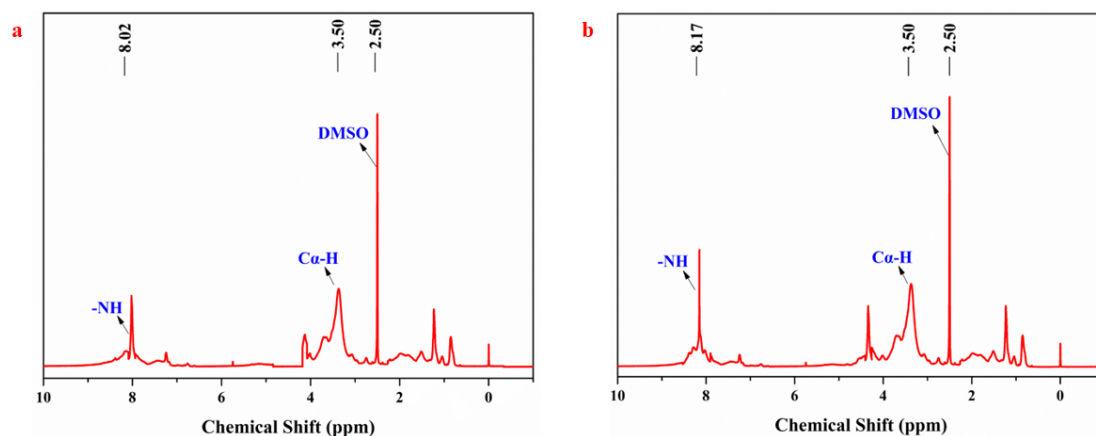
**Figure S1.** Photographs of the dissolution of collagen over a range of concentrations (0% ~ 9%, w/w) using different solvents at 4 °C. (a) Formic acid. (b) The DES of ZnCl<sub>2</sub>:FA(1:5). (c) The DES of U:LA(1:2).



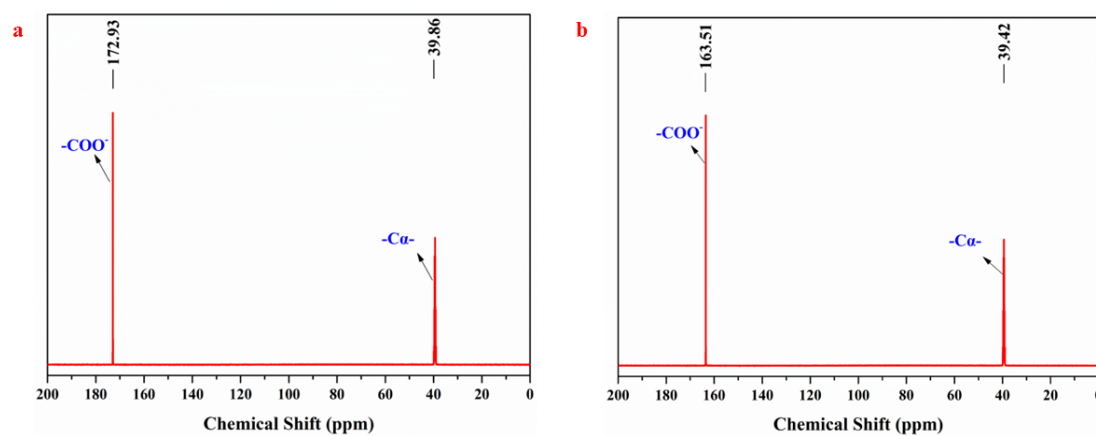
**Figure S2.** The melting points of the DESs of ZnCl<sub>2</sub>:FA(1:5) with different water contents.



**Figure S3.** The regeneration rates of collagen obtained by using the immersion method in different precipitants (water, ethanol, and acetone) and the dialysis method.



**Figure S4.** The  $^1\text{H}$  NMR spectra of (a) the original collagen and (b) the DES-collagen solution.



**Figure S5.** The  $^{13}\text{C}$  NMR spectra of (a) the original collagen and (b) the DES-collagen solution.

**Table S1.** Comparison of the solubility of collagen in different solvent systems.

Solvents	Temperature (°C)	Solubility (wt%)	Reference
EG: ZnCl <sub>2</sub> (4:1)	45	11	
EG: ZnCl <sub>2</sub> (4:1) + HCl	45	16.6	
EG: ZnCl <sub>2</sub> (4:1)	70	18.5	13
EG: ZnCl <sub>2</sub> (4:1) + HCl	70	17	
EG: ZnCl <sub>2</sub> (4:1)	90	21	
EG: ZnCl <sub>2</sub> (4:1) + HCl	90	22.5	
(EMIM)(Ac)/Na <sub>2</sub> HPO <sub>4</sub>	25	3.9	
(EMIM)(Ac)/Na <sub>2</sub> HPO <sub>4</sub>	30	5.5	
(EMIM)(Ac)/Na <sub>2</sub> HPO <sub>4</sub>	35	6.5	19
(EMIM)(Ac)/Na <sub>2</sub> HPO <sub>4</sub>	40	7.8	
(EMIM)(Ac)/Na <sub>2</sub> HPO <sub>4</sub>	45	10.5	
TBAH/DMSO/H <sub>2</sub> O	25	10.25	21
Urea/HAc	-12	12	11
NaAc/HAc (pH 3.0)	25	10	8
ZnCl <sub>2</sub> :FA(1:5) containing 40% (w/w) water	4	27.4	This work

EG: ethylene glycol; (EMIM)(Ac): 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]); TBAH: tetra-*n*-butylammonium hydroxide; HAc: acetic acid; FA: formic acid

**Table S2.** The FTIR spectra peak positions and the absorption ratios between the Amide III and 1450 cm<sup>-1</sup> peaks of the regenerated collagens from the dissolution of collagen in the DESs with different water contents, in comparison with those of the original collagen.

Collagen sample	Wavenumber of characteristic peak (cm <sup>-1</sup> )					$A_{(\text{amide III})}/A_{1450}$
	Amide A	Amide B	Amide I	Amide II	Amide III	
C	3329	2930	1660	1555	1240	1.01
30	3330	2930	1660	1550	1242	1.03
40	3330	2929	1660	1550	1240	1.02
50	3332	2926	1654	1549	1235	1.04

C: the original collagen; 30, 40, and 50: the regenerated collagens from the dissolution of collagen in the DESs of ZnCl<sub>2</sub>:FA(1:5) containing 30%, 40%, and 50% (w/w) water, respectively.

**Table S3.** The absorption ratios between the positive and negative peaks (Rpn) of the CD spectra of the regenerated collagens from the dissolution of collagen in the DESs with different water contents, in comparison with that of the original collagen.

Collagen sample	Rpn
C	0.121
30	0.051
40	0.063
50	0.002

C: the original collagen; 30, 40, and 50: the regenerated collagens from the dissolution of collagen in the DESs of ZnCl<sub>2</sub>:FA(1:5) containing 30%, 40%, and 50% (w/w) water, respectively.

**Table S4.** The FTIR spectra peak positions and the absorption ratios between the Amide III and 1450 cm<sup>-1</sup> peaks of the regenerated collagens from the dissolution of collagen in the DES of ZnCl<sub>2</sub>:FA(1:5) containing 40% (w/w) water for different periods of time, in comparison with those of the original collagen.

Collagen sample	Wavenumber of characteristic peak (cm <sup>-1</sup> )					A <sub>(amide III)</sub> /A <sub>1450</sub>
	Amide A	Amide B	Amide I	Amide II	Amide III	
C	3329	2930	1660	1555	1240	1.01
0	3330	2930	1660	1550	1240	1.02
8h	3330	2929	1660	1550	1240	1.03
16h	3331	2928	1658	1549	1238	1.04
1d	3332	2932	1660	1552	1240	1.04
2d	3330	2930	1660	1550	1242	1.05
4d	3330	2929	1662	1550	1240	1.07
8d	3331	2928	1659	1549	1239	1.07
16d	3332	2930	1660	1550	1240	1.08
32d	3331	2929	1658	1549	1237	1.10

C: the original collagen; 0: the regenerated collagen immediately after the dissolution of collagen in the DES; 8h, 16h, 1d, 2d, 4d, 8d, 16d, 32d: the regenerated collagens from the dissolution of collagen in the DES for 8 hours, 16 hours, 1 day, 2 days, 4 days, 8 days, 16 days, and 32 days, respectively.

**Table S5.** The absorption ratios between the positive and negative peaks (Rpn) of the CD spectra of the regenerated collagens from the dissolution of collagen in the DES of ZnCl<sub>2</sub>:FA(1:5) containing 40% (w/w) water for different periods of time, in comparison with that of the original collagen.

Collagen sample	Rpn
C	0.121
0	0.063
8h	0.056
16h	0.050
1d	0.046
2d	0.040
4d	0.034
8d	0.029
16d	0.016
32d	—

C: the original collagen; 0: the regenerated collagen immediately after the dissolution of collagen in the DES; 8h, 16h, 1d, 2d, 4d, 8d, 16d, 32d: the regenerated collagens from the dissolution of collagen in the DES for 8 hours, 16 hours, 1 day, 2 days, 4 days, 8 days, 16 days, and 32 days, respectively.

**Table S6.** The thermal denaturation temperature ( $T_d$ ) values of the regenerated collagens from the dissolution of collagen in the DES of  $ZnCl_2:FA(1:5)$  containing 40% (w/w) water for different periods of time, in comparison with that of the original collagen.

Collagen sample	$T_d$ (°C)
C	$73.0 \pm 0.2$
0	$71.6 \pm 0.3$
8h	$70.5 \pm 0.4$
16h	$69.5 \pm 0.2$
1d	$68.6 \pm 0.2$
2d	$66.4 \pm 0.3$
4d	$64.6 \pm 0.2$
8d	$63.2 \pm 0.3$
16d	$62.4 \pm 0.3$
32d	$61.1 \pm 0.2$

C: the original collagen; 0: the regenerated collagen immediately after the dissolution of collagen in the DES; 8h, 16h, 1d, 2d, 4d, 8d, 16d, 32d: the regenerated collagens from the dissolution of collagen in the DES for 8 hours, 16 hours, 1 day, 2 days, 4 days, 8 days, 16 days, and 32 days,

**Table S7.** The content of Zn in the regenerated collagen films prepared under different dialysis times.

Collagen films	Content of Zn (% w/w)
A	$0.166 \pm 0.0014$
B	$0.062 \pm 0.0006$
C	$0.017 \pm 0.0004$
D	$0.003 \pm 0.0002$

A, B, C, and D: the regenerated collagen films derived from the collagen solutions dissolved in the DES of  $ZnCl_2:FA(1:5)$  containing 40% (w/w) water and dialysed for 1, 2, 3, and 4 days, respectively.