

Supporting Information

Hydrogen bond reconstruction strategy of eutectic solvents that realizes room temperature dissolution of cellulose

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Notes

Note S1. Measurement for binding energy of hydrogen bonds of formic acid.

In previous study of Luo et al^[1], they proposed a linear formula (1) for determining the hydrogen bonding energy via ¹H NMR chemical shift of proton, revealing that the compensated natural logarithm of the chemical shift ($\ln\delta + \Delta\delta$) is linearly correlated with $1/T$.

$$\ln\delta + \Delta\delta = \frac{A}{R} \frac{1}{T} + B \quad (1)$$

where $\Delta\delta = \ln\left(1 - \frac{\delta_0}{\delta}\right) - 2\ln\left(1 - \frac{\delta}{\delta_\infty}\right)$, $A = -\frac{E_{binding}}{R}$, and $B = -\ln\frac{\delta_\infty - \delta_0}{2A_{Arrhenius}C_0\delta_\infty^2}$

In addition, according to the theory “continuous association of hydrogen-bonds”, an experimental COOH proton chemical shift δ and the concentration of the carboxyl compound monomer C satisfied the linear equation (2):

$$\delta = \delta_\infty - \frac{\delta_\infty - \delta_0}{C_0} \times C \quad (2)$$

δ_∞ is the ideal ¹H chemical shift of completed H-bonded COOH proton, and δ_0 is the ideal ¹H chemical shift of “free” COOH proton that does not form the hydrogen bonds, C_0 is the analytical concentration of the carboxyl compound and satisfied the equation (3):

$$(K_1K_2 - K_2^2)C^3 - (2K_1 - 2K_2 - K_2^2C_0)C^2 - (2K_2C_0 + 1)C + C_0 = 0 \quad (3)$$

Meanwhile, δ and C satisfied the equation (1) and equation (4) could be deduced:

$$\delta = \delta_\infty - \frac{\delta_\infty - \delta_0}{C_0} \left[\frac{2c}{3a} + 2 \sqrt{\left(\frac{3ab + 4c^2}{9a^2}\right) \cos\left\{ \frac{1}{3} \cos^{-1} \frac{\left(\frac{8c^3}{27} - \frac{a^2}{2C_0} + \frac{abc}{3}\right)}{\left(\frac{ab}{3} + \frac{4c^2}{9}\right)^{3/2}} - \frac{2\pi}{3} \right\}} \right] \quad (4)$$

Where $a = K_1K_2 - K_2^2$, $b = 2K_2C_0 + 1$, and $c = K_1 - K_2 - \frac{K_2^2C_0}{2}$.

To determine the δ_0 , δ_∞ , K_1 , K_2 , ΔG_1 and $\Delta E_{HB,1}$ (binding energy of FA dimer), the concentration and temperature dependence of the ¹H NMR shift of COOH in FA were

implemented in the weak HBA solvent CDCl₃. Furthermore, in accordance with the results in **Table S4** and **Figure S1a,b**, Origin 2018 software was employed to fit the curve as shown in **Figure 1c,d**, and the parameters (δ_0 , δ_∞ , K_1 , K_2 , ΔG_1 and $\Delta E_{HB,1}$) were enumerated in **Table S5**. K_1 is 4 orders of magnitude large than K_2 , hence we can speculate that the intermolecular HBs almost only exist dimer form of FA. The binding energy (BE) value for FA dimer is -8.258 kcal·mol⁻¹.

Note S2. Measurement for binding energy between HBA and HBD.

In previous study of Luo, Y., et al^[2], they proposed a linear formula (5) for determining the association constant K for the reversible process that forms HBD···HBA between monomer HBD and molecular HBA.

$$\frac{1}{\Delta\delta} = \frac{a}{K} \cdot \frac{1}{C} + a \quad (5)$$

1/ $\Delta\delta$ is the reciprocal of the proton chemical shift changes and 1/ C is the reciprocal of the proton-acceptor concentration. They also developed experimental method to determine the hydrogen bonds binding energy (E_{HB}) by a linear equation (6) as a function of the natural logarithm of chemical shifts.

$$\ln\delta + \sigma_\delta = -\frac{E_{HB}}{RT} + A \quad (6)$$

Where the compensated term σ_δ at different temperature could be obtained according to equation (7):

$$\sigma_\delta = \ln\left[\frac{\delta_{DA} - \delta_D}{\delta \cdot (\delta - \delta_0)} \cdot \frac{C_D}{C_{D_0}} \cdot C - \frac{1}{\delta} \cdot C\right] \quad (7)$$

In the light of the ¹H NMR experimental data in **Tables S6** and **S7** and **Figures S4-S9**, Origin 2018 software was employed to fit the curve as shown in **Figures S2** and **S3**.

Note S3. Calculation of Huggins constant^[3].

From the perspective of thermodynamic, intrinsic viscosity $[\eta]$ is one of the important parameters to reflect the solubility of a solvent, and its value can be calculated by equations (8) and (9):

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} \quad (8)$$

$$[\eta] = \lim_{C \rightarrow 0} \left(\frac{\eta_{sp}}{C} \right) \quad (9)$$

Where η_{sp} and η are the specific viscosity and viscosity of solutions, and η_s is the viscosity of the pure solvent. C is the concentration of solution.

The Huggins-equation is a truncated version of equation (10) and is defined as follows:

$$\eta_{sp} = C \cdot [\eta] + K_H \cdot (C \cdot [\eta])^2 + A \cdot (C \cdot [\eta])^n \quad (10)$$

Where K_H is the Huggins constant, A and n are obtained from the non-linear regression.

Note S4. Determination of the formyl group content and DS of regenerated formate cellulose.

The content of formyl groups in the regenerated formate cellulose was measured according to the calcium acetate method.^[4] Firstly, 50 grams of deionized water and 30 grams of 0.25 M calcium acetate solution were mixed in a flask and then 0.5 gram of regenerated formate cellulose was added. After reaction for 12 hours with continuously shaking, 30 grams of the dispersion liquid was titrated with 0.01 M sodium hydroxide using a phenolphthalein indicator. Then, the formyl contents were calculated according to the formula (11):

$$\text{Formyl content (mmol/g)} = \frac{\frac{50 + 30 + 0.5}{30} \times 0.01 \times V_{NaOH}}{m} \quad (11)$$

Where 0.01 is the molar concentration (mol/L) of NaOH, V_{NaOH} is the volume (mL) of NaOH solution used for titration, and m is the weight (gram) of regenerated formate cellulose.

The degree of substitution (DS) values of the regenerated formate cellulose were

determined according to the back-titration method.^[5] The regenerated formate cellulose (0.3 g) was mixed with 0.2 M potassium hydroxide in 50% aqueous alcohol (30 mL) in a conical flask. Then, the flask was shaken at 120 rpm at room temperature for 24 hours. After that, 0.2 M hydrochloric acid (30 mL) was added. A further half an hour later, the solution was titrated with 0.1 M sodium hydroxide, and phenolphthalein was used as an indicator. The formyl content was calculated by the formula (12), and then the DS value was calculated by the formula (13). Native cellulose was also carried out using the same procedures as a blank.

$$Formyl (\%) = \frac{(V_S - V_B) \times N_{NaOH} \times M_{formyl} \times 10^{-3} \times 100}{W}$$

(12)

$$DS = \frac{162 \times Formyl\%}{M_{formyl} \times 100 - ((M_{formyl} - 1) \times Formyl\%)}$$

(13)

Here, V_B (mL) is the volume of NaOH required for titration of the blank, V_S (mL) is the volume of NaOH required to titrate the regenerated formate cellulose, N_{NaOH} is the normality of the NaOH solution, M_{formyl} is the molecular weight of the formyl group (29 g/mol), W is the mass of sample used, and 162 is the molecular weight of the anhydroglucose units.

Note S5. The process of regenerating cellulose and recycling solvent.

Water was added to the dissolved cellulose mixture solution (10:1), and the mixture was stirred for around twenty minutes. The precipitated cellulose was filtrated and putted it into a vacuum drying oven 60 °C for 12 hours. The excess water was removed using rotary evaporator. Finally, we obtain the regenerated formate cellulose and recycled DES. In consideration of FA tends to be evaporated with water, the loss of FA is approximate 2–3 grams, so pristine solvent (DES) is used to make up for it.

Note S6. The preparation of hydrogel.

The cellulose dissolved solution was centrifuged at 5000 rpm for 5 minutes to remove

the bubbles, and the solution was evenly poured into petri dish, then 30 wt% calcium chloride aqueous solution was added and soaked for about 4–5 hours. Take out the sample and then soak it in ethanol for about 1–2 hours to obtain the regenerated formate cellulose hydrogel.

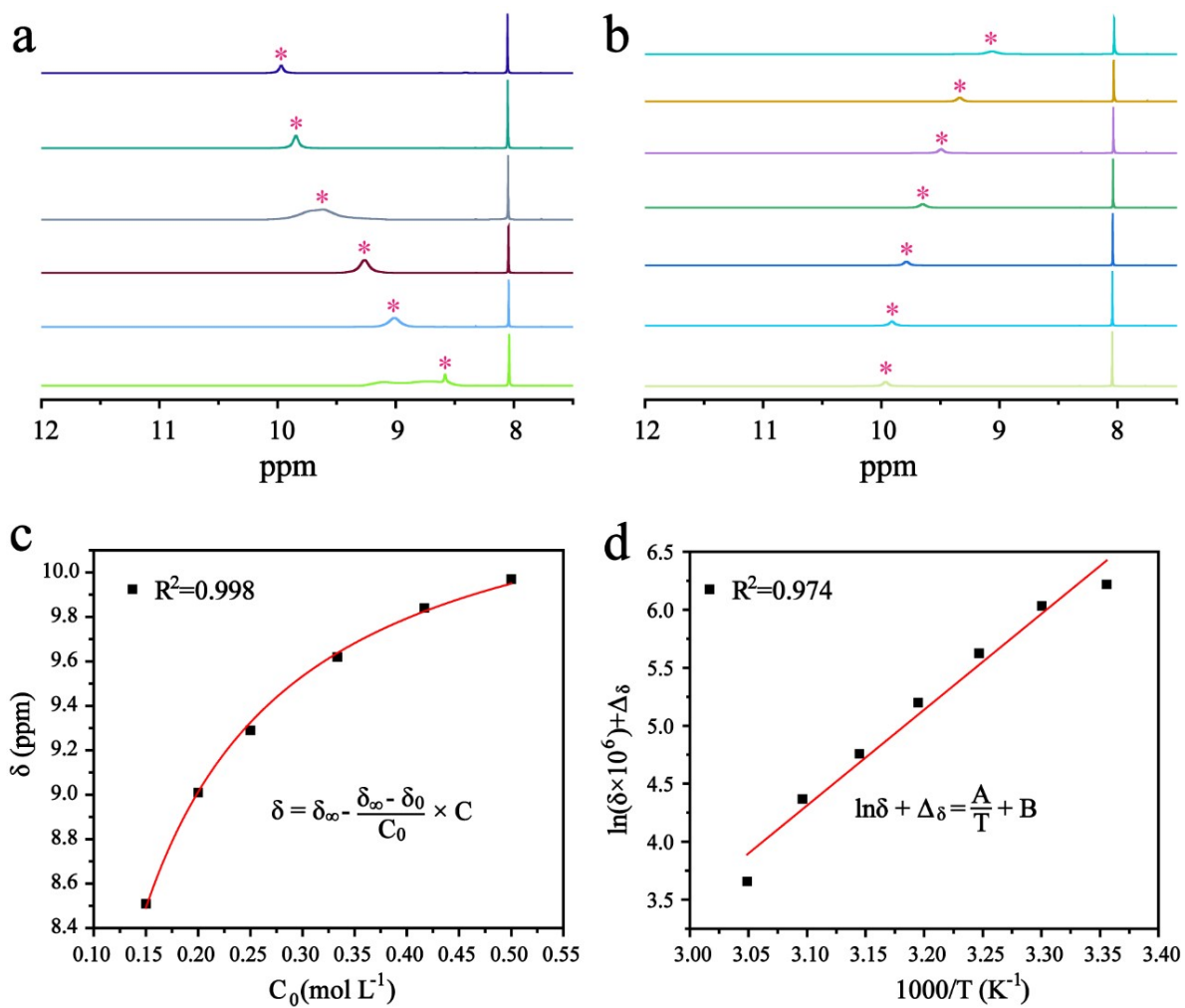


Figure S1 (a) Concentration and (b) temperature dependence experiment of ^1H NMR spectra of FA in CDCl_3 . (c) Concentration dependence of the ^1H NMR shift of COOH in FA in CDCl_3 . (d) Plot of $1/T$ versus $\ln \delta + \Delta \delta$ of COOH protons for FA.

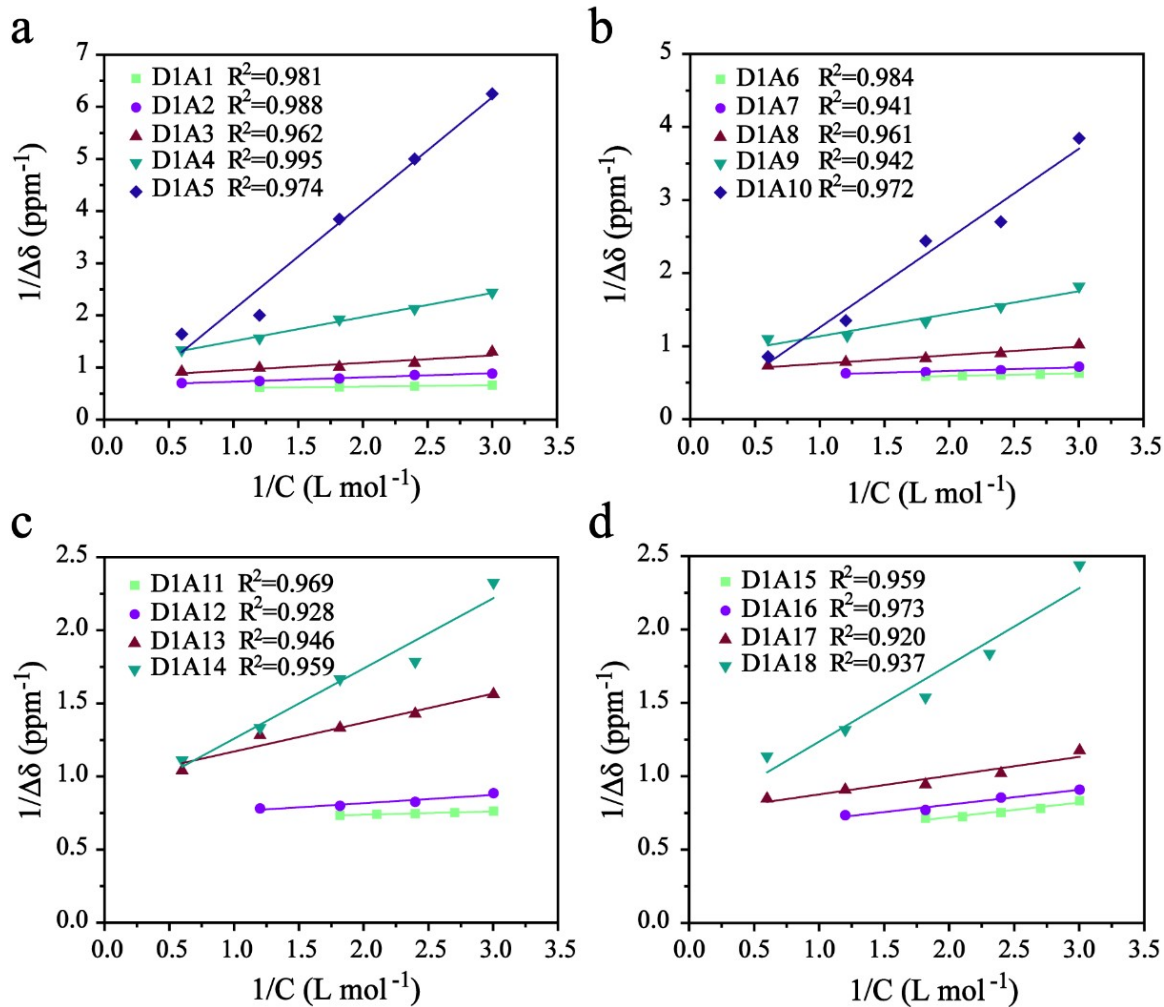


Figure S2 Plot of $1/C$ versus $1/\Delta\delta$ for D1-*An* couples.

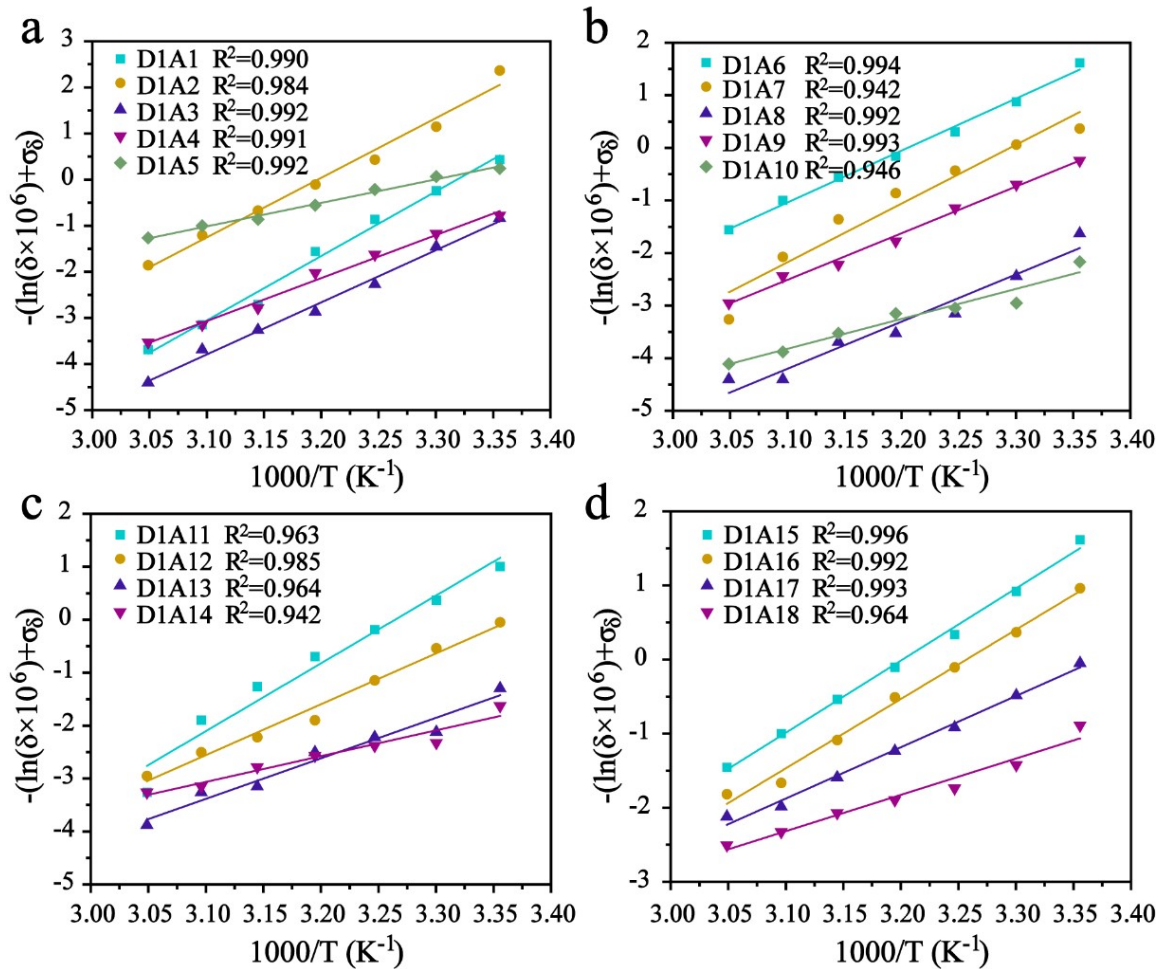


Figure S3 Plot of $1000/T$ versus $-(\ln(\delta \times 10^6) + \sigma_\delta)$ for D1-An couples.

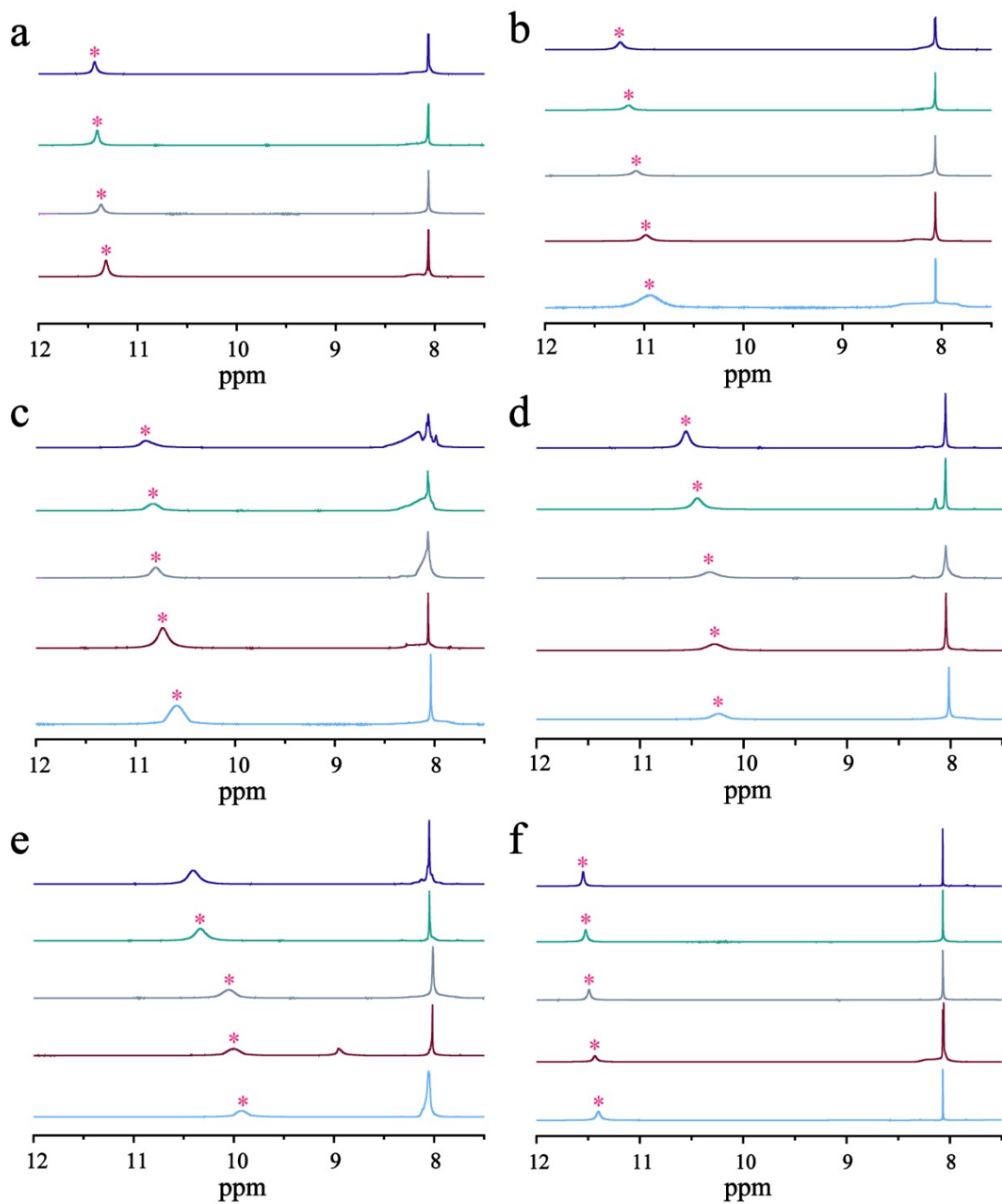


Figure S4 Concentration dependence experiment of ^1H NMR spectra of D1 with (a) A1, (b) A2, (c) A3, (d) A4, (e) A5, and (f) A6 in CDCl_3 .

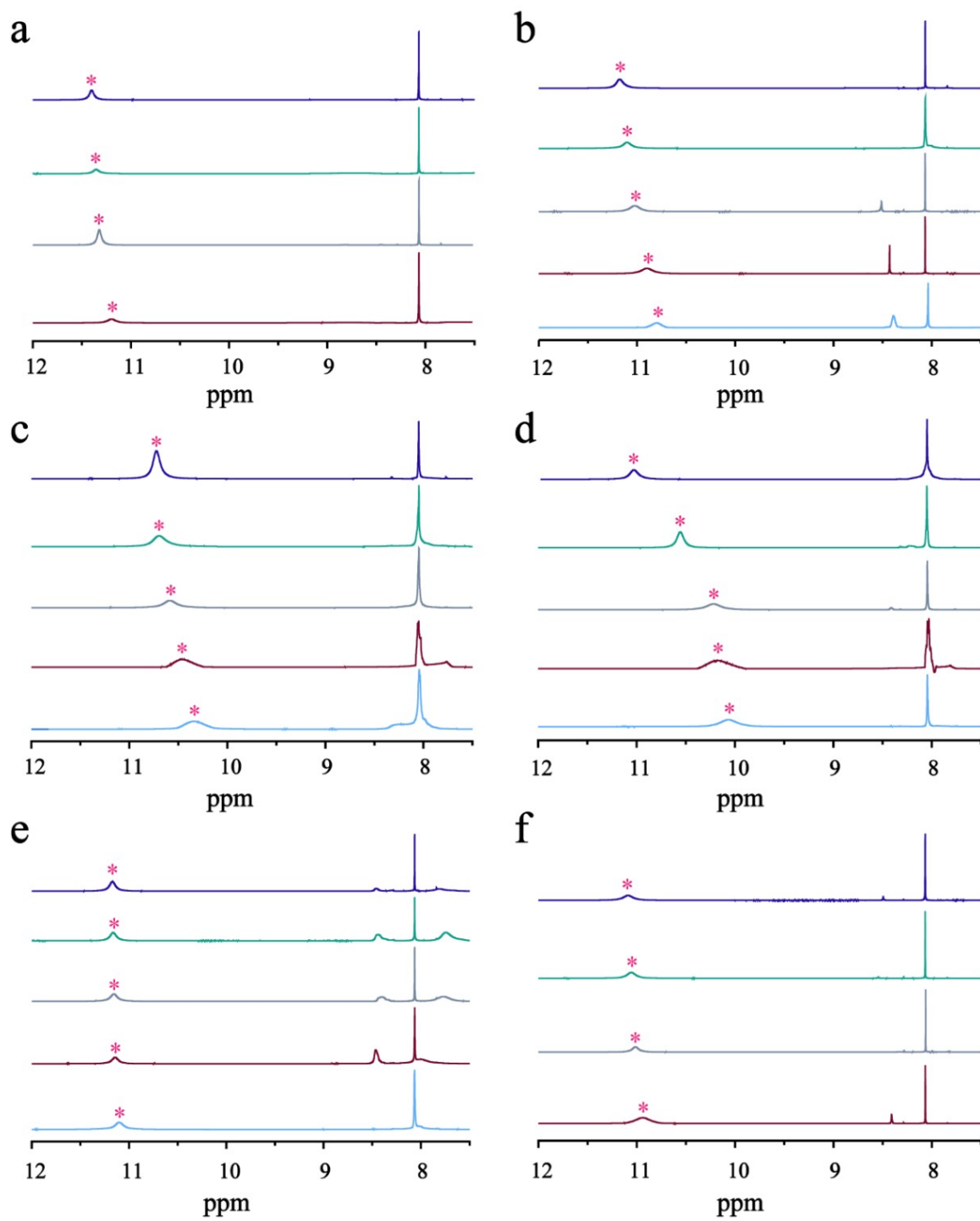


Figure S5 Concentration dependence experiment of ^1H NMR spectra of D1 with (a) A7, (b) A8, (c) A9, (d) A10, (e) A11, and (f) A12 in CDCl_3 .

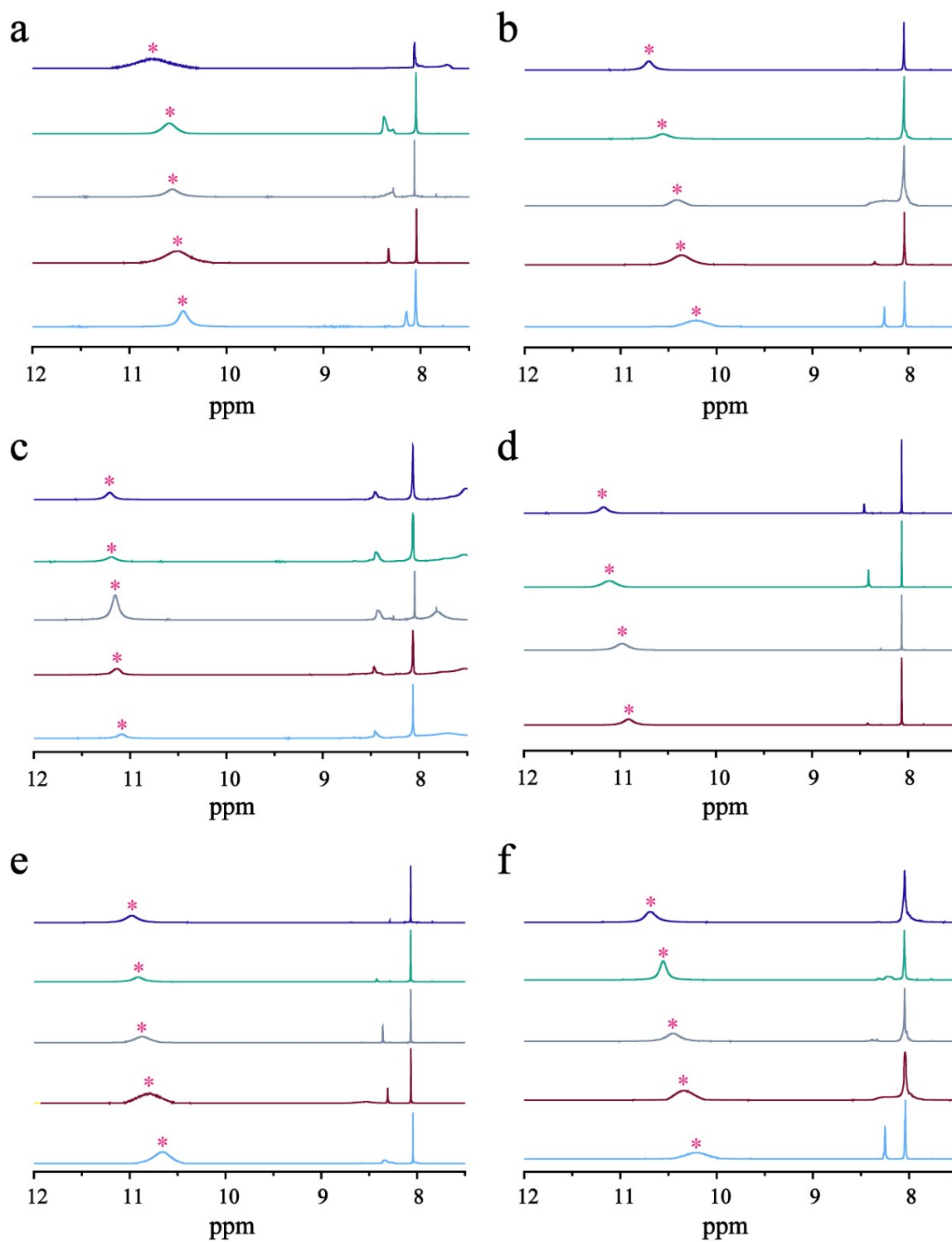


Figure S6 Concentration dependence experiment of ^1H NMR spectra of D1 with (a) A13, (b) A14, (c) A15, (d) A16, (e) A17, and (f) A18 in CDCl_3 .

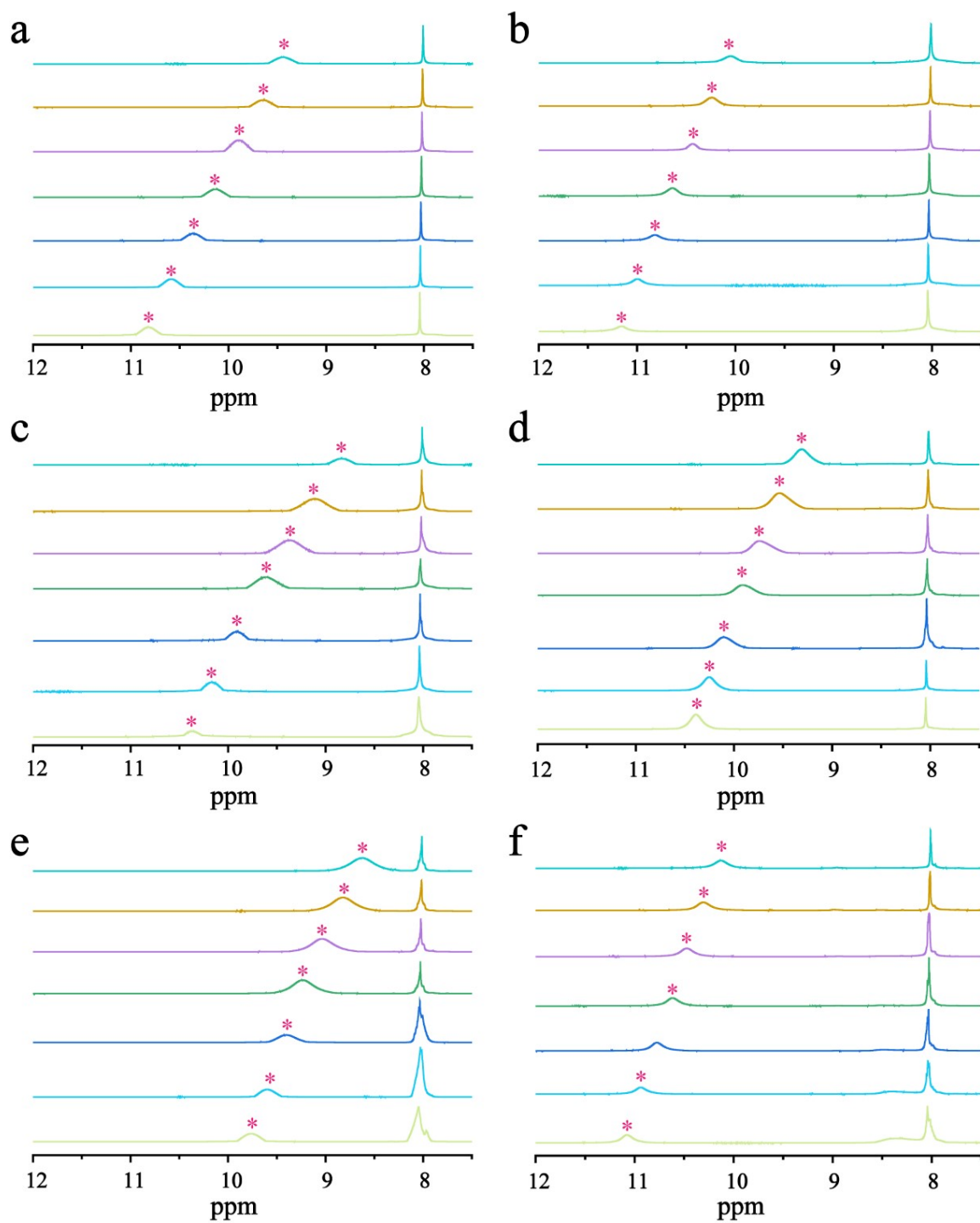


Figure S7 Temperature dependence experiment of ^1H NMR spectra of D1 with (a) A1, (b) A2, (c) A3, (d) A4, (e) A5, and (f) A6 in CDCl_3 .

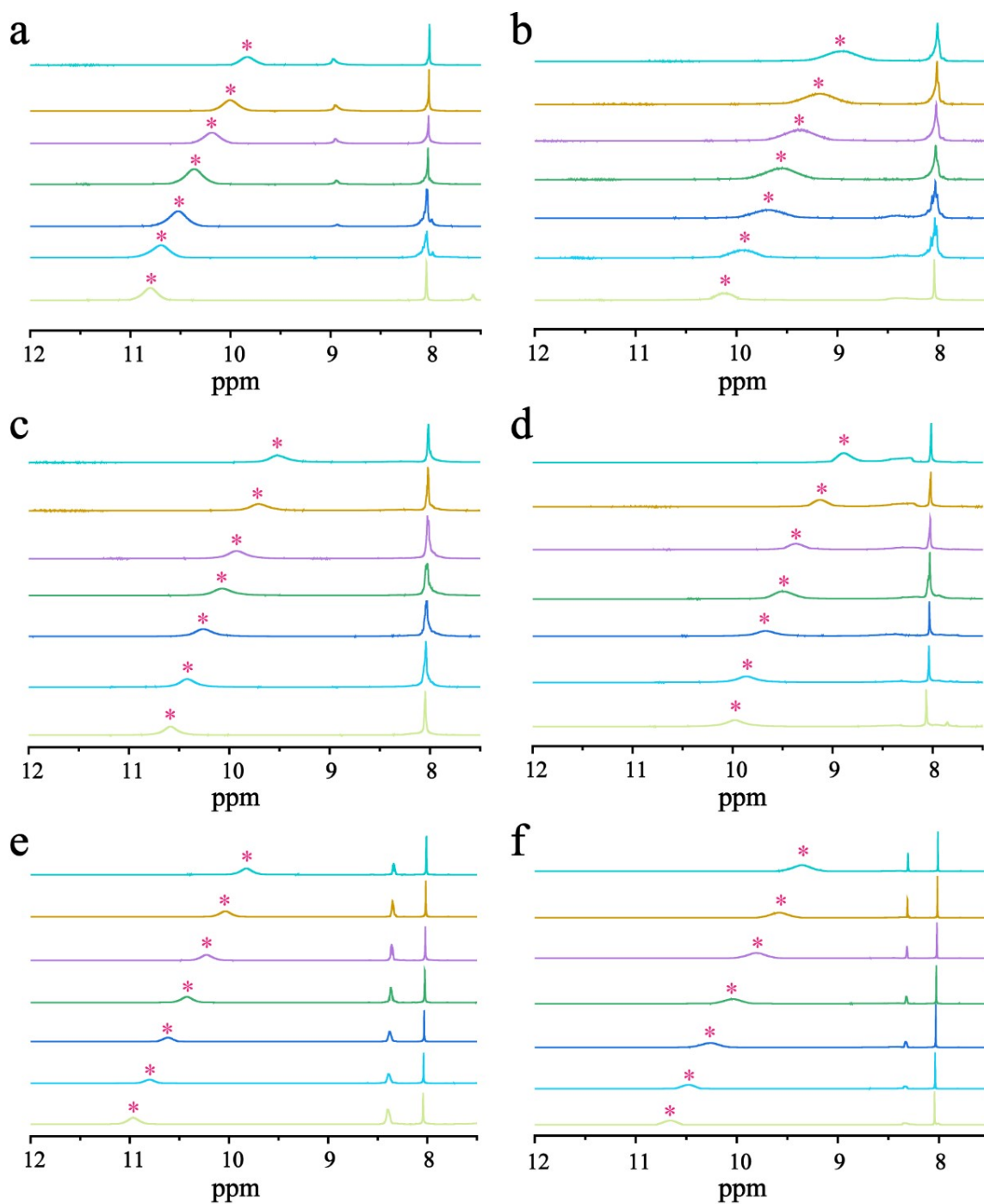


Figure S8 Temperature dependence experiment of ^1H NMR spectra of D1 with (a) A7, (b) A8, (c) A9, (d) A10, (e) A11, and (f) A12 in CDCl_3 .

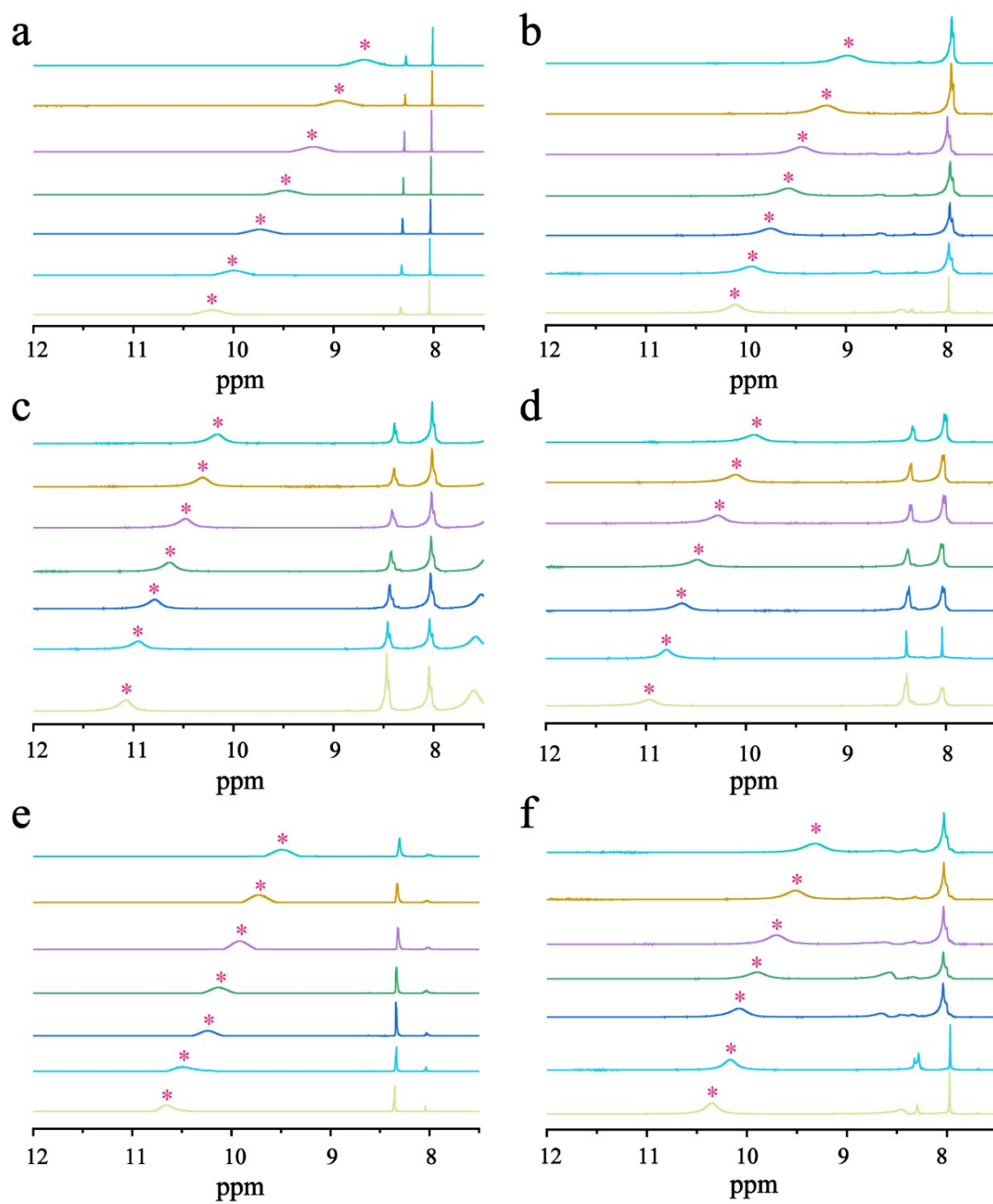


Figure S9 Temperature dependence experiment of ^1H NMR spectra of D1 with (a) A13, (b) A14, (c) A15, (d) A16, (e) A17, and (f) A18 in CDCl_3 .

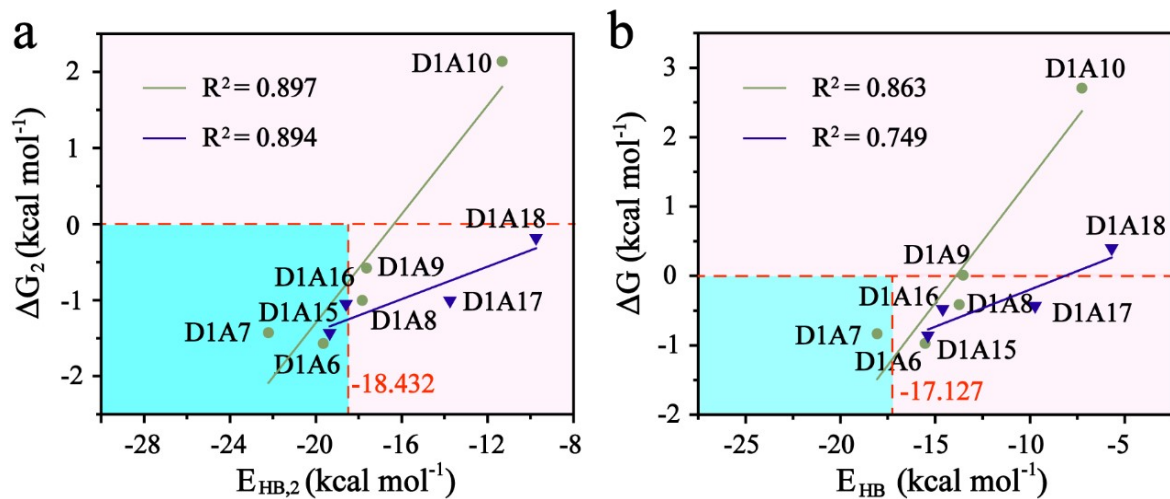


Figure S10 (a) Relationship of ¹H NMR fit the curve calculated $E_{HB,2}$ and ΔG_2 for D1-*An*

couples. (b) The relationship between E_{HB} and ΔG of D1-*An* couples.

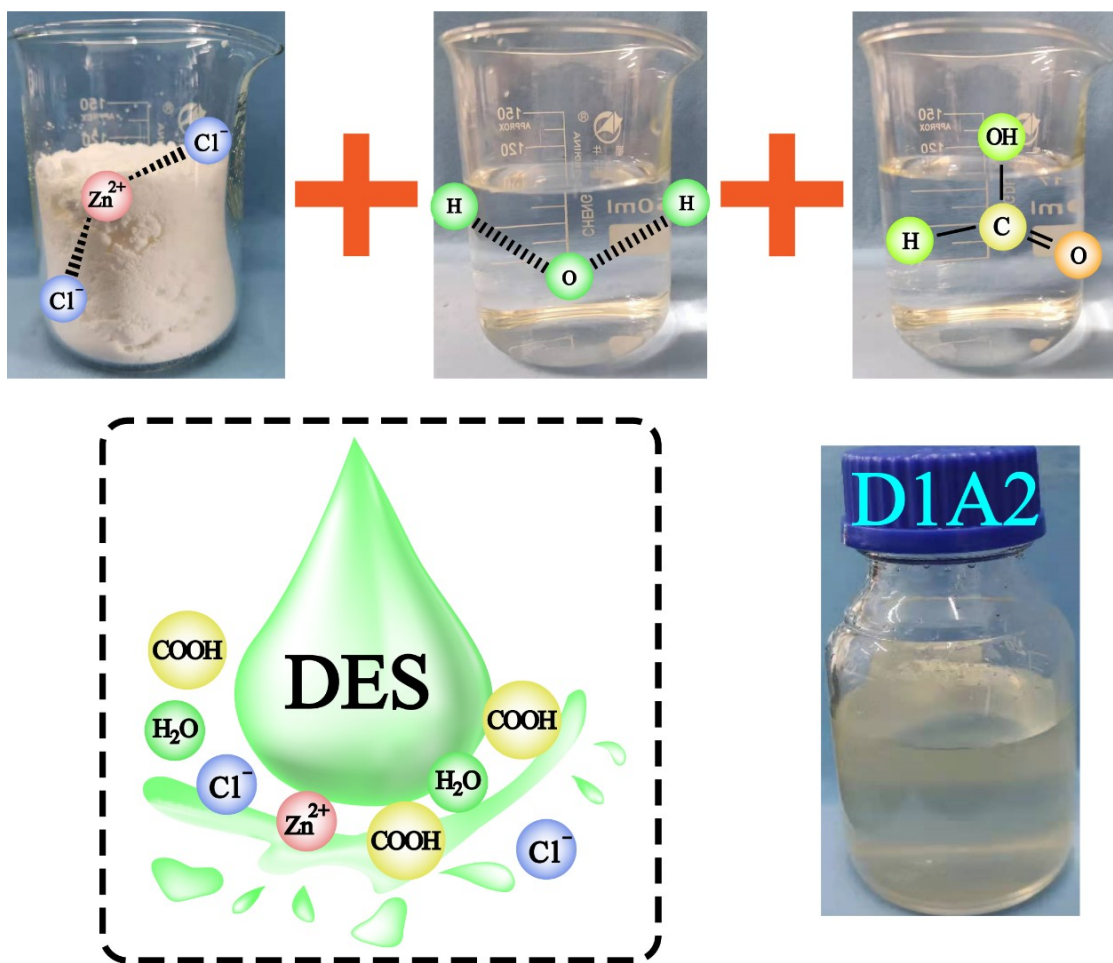


Figure S11 Illustration of the synthesis process of the eutectic solvent D1A2.

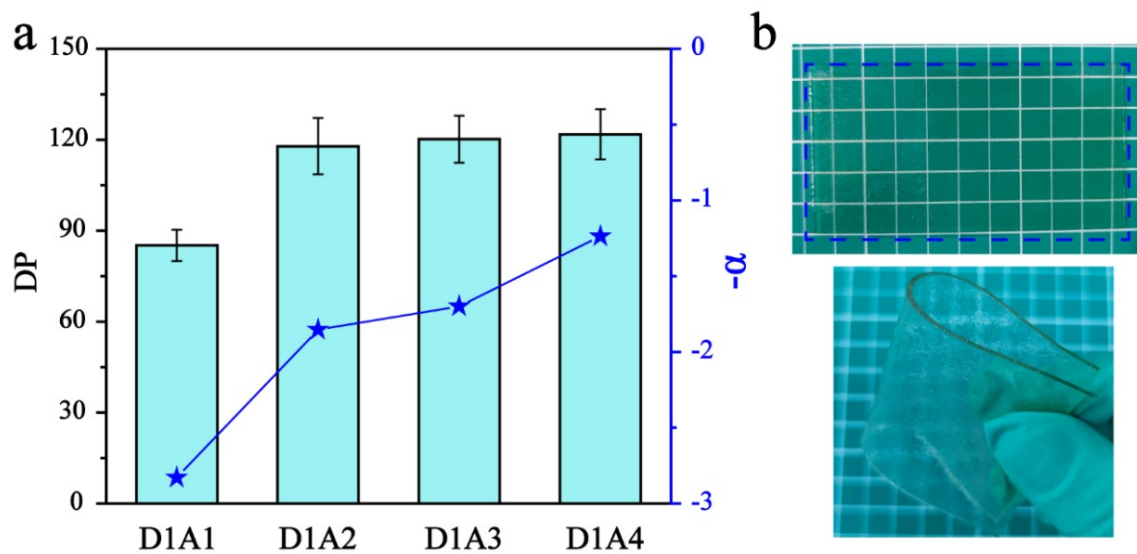


Figure S12 (a) Dependence of DP of the regenerated formate cellulose on α for different combination of HBA and HBD. (b) Photographic images of preparation of transparent hydrogel.

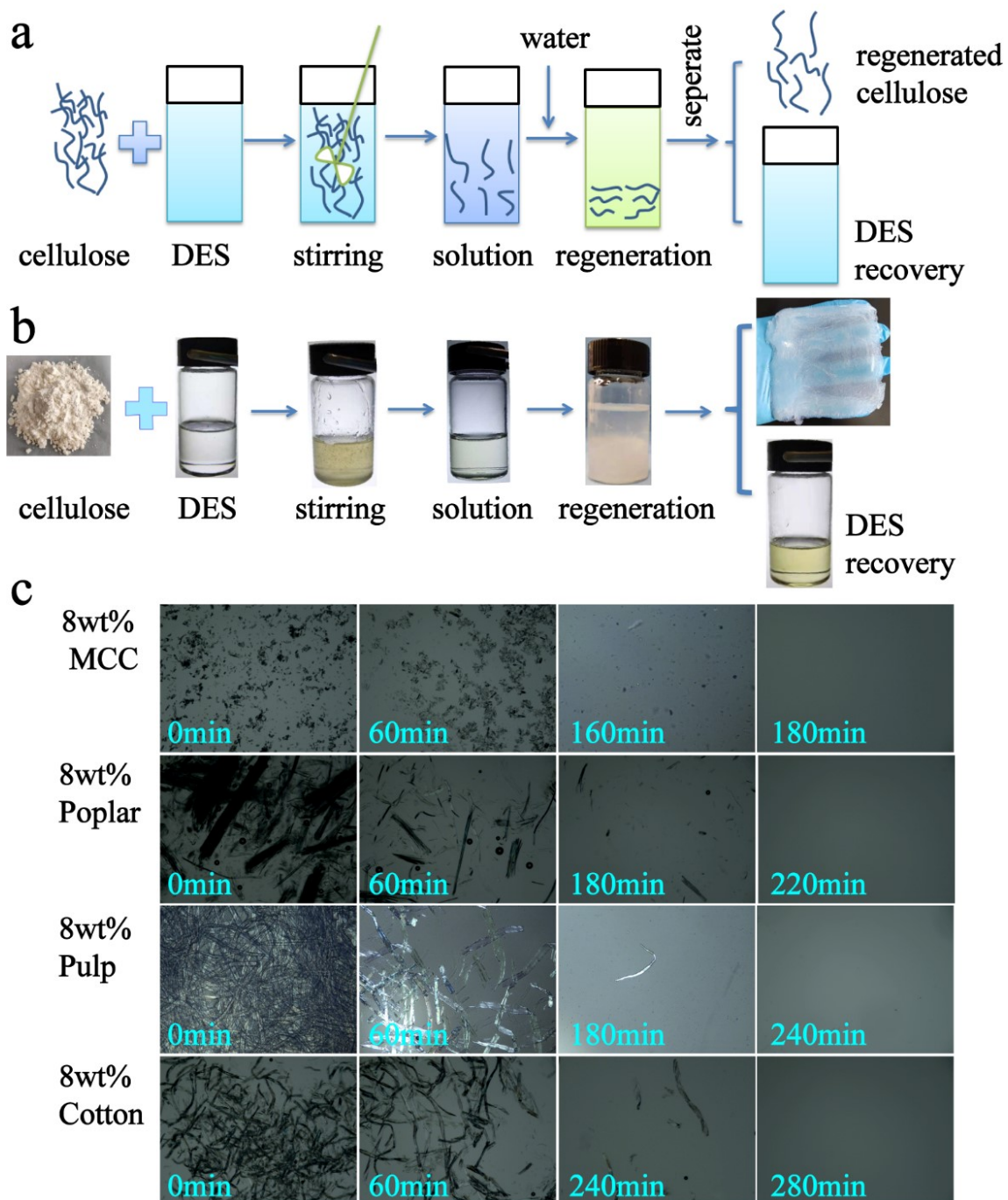


Figure S13 (a) Flow chart and (b) photographic images of the dissolving biomass process using the D1A2 and regenerating cellulose using water. (c) Micrographs of MCC, Poplar, pulp and cotton dissolved by the D1A2 at room temperature.

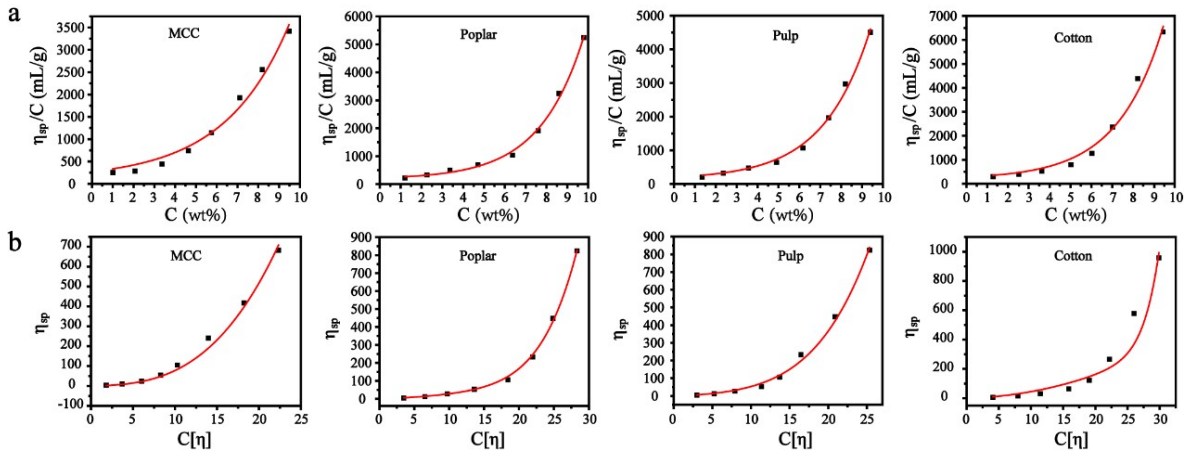


Figure S14 (a) Concentration dependence of η_{sp}/C for cellulose/solvent solution at room temperature. (b) The specific viscosity (η_{sp}), as a function of $C[\eta]$ for cellulose/solvent solution at room temperature.

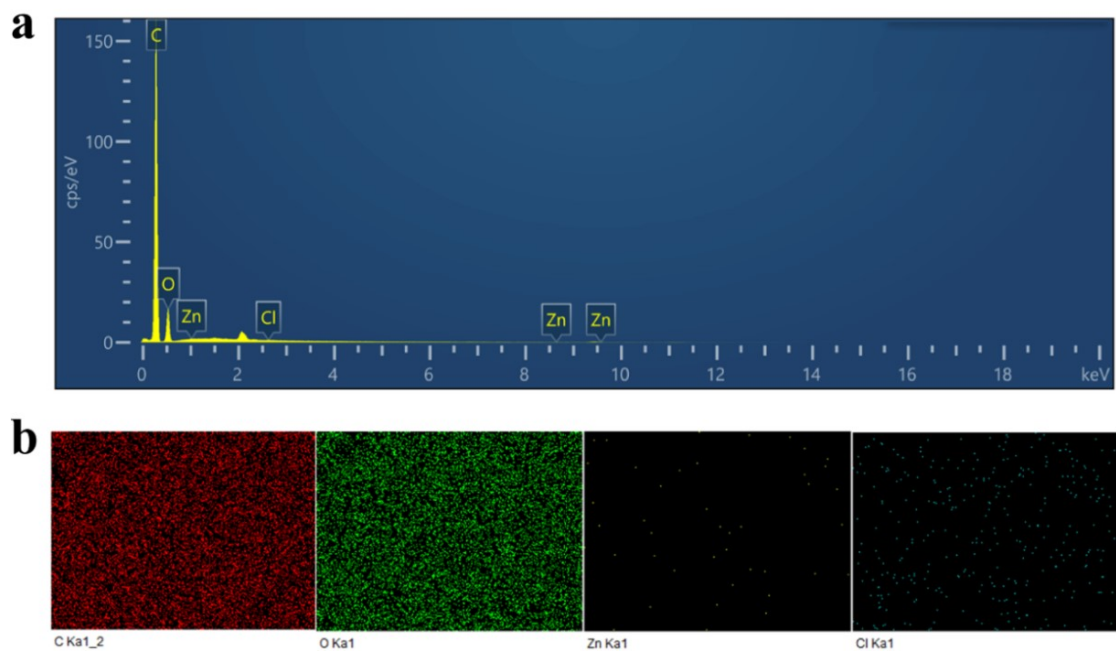


Figure S15 (a) The distribution of elements in EDX spectrum. (b) EDX elemental (C, O, Zn, and Cl) mapping images of the regenerated formate cellulose (magnification: $\times 5000$).

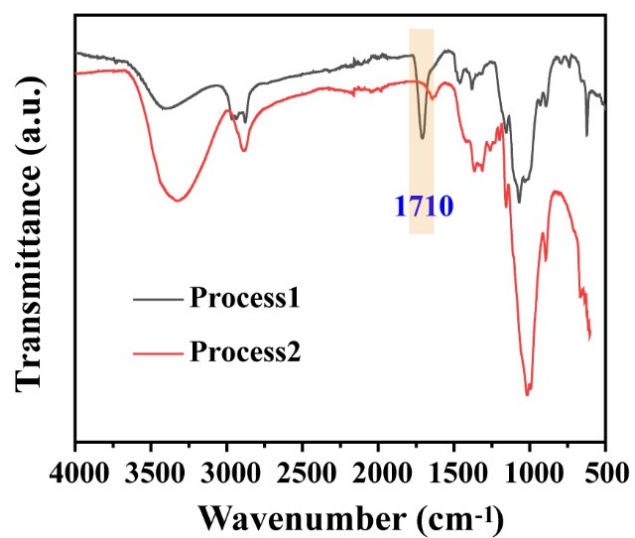


Figure S16 FTIR spectra of the regenerated formate cellulose (process 1) and that after boiling in water for 6 hours (process 2).

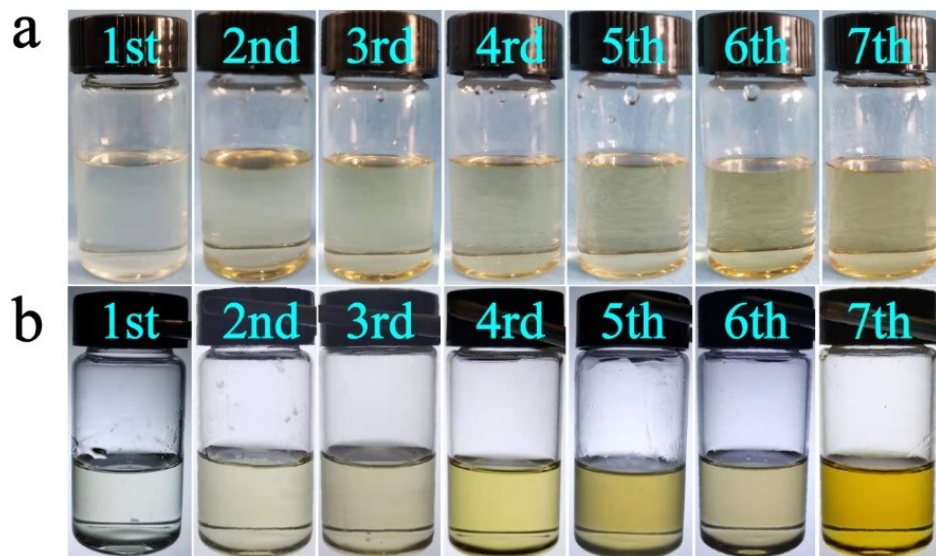


Figure S17 Photographic pictures of (a) the D1A2 solvent after seven successive recycles and (b) their corresponding dissolved cellulose solutions.

Table S1 Properties of four types of cellulose feedstocks [6].

Parameters	MCC	Wood cellulose	Pulp cellulose	Cotton linters
Degree of polymerization	183	717	1539	2243
Average molecular weight	2.96×10^4	1.16×10^5	2.49×10^5	3.63×10^5
Content of α -cellulose	98.31%	95.75%	93.90%	99.97%
Content of hemicellulose	1.73%	3.89%	5.90%	–
Content of lignin	–	0.36%	0.20%	0.03%
Crystallinity index	62.12%	62.41%	53.58%	60.72%

Table S2 The binding energy (BE) and pKa ^[7] of formic acid (FA), acetic acid (AA), lactic acid (LA), methanol (MA), and methanamide (ME).

HBD	BE (kcal mol ⁻¹)	pKa
FA	-7.196	3.75
AA	-10.279	4.76
LA	-16.876	3.86
MA	-8.946	15.5
ME	-6.826	23.5

Table S3 Concentration dependent and temperature dependent experiments of FA.

Concentration variation experiments		Temperature variation experiments	
C (mol L ⁻¹)	δ (ppm)	T (K)	δ (ppm)
0.150	8.51	298	9.96
0.200	9.01	303	9.91
0.250	9.26	308	9.79
0.333	9.62	313	9.65
0.417	9.84	318	9.49
0.500	9.97	323	9.34
		328	9.06

Table S4 Parameters of formic acid determined by concentration variation and temperature variation experiments at 296K.

Concentration variation experiments				
δ_0 (ppm)	δ_∞ (ppm)	K_1 (L mol ⁻¹)	K_2 (L mol ⁻¹)	ΔG_1 (kcal mol ⁻¹)
8.263	10.575	2.665	9.482×10 ⁻⁴	-0.577
Temperature variation experiments				
$E_{HB,1}$ (kcal mol ⁻¹)	ΔS_1 (cal mol ⁻¹)	ΔG_{T1} (kcal mol ⁻¹)		
-8.258	-21.286	-1.957		

Table S5 Concentration dependence experiment of D1 with A1-A18. (stock [D1] = 1 mmol)

D1A1	C (A1) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	11.32	1.51	0.662
	0.417	2.398	11.37	1.56	0.641
	0.550	1.818	11.41	1.60	0.625
	0.833	1.200	11.44	1.63	0.613
D1A2	C (A2) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.94	1.13	0.885
	0.417	2.398	10.98	1.17	0.855
	0.550	1.818	11.08	1.27	0.787
	0.833	1.200	11.16	1.35	0.741
	1.667	0.600	11.24	1.43	0.699
D1A3	C (A3) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.58	0.77	1.299
	0.417	2.398	10.73	0.92	1.087
	0.550	1.818	10.80	0.99	1.010
	0.833	1.200	10.82	1.01	0.990
	1.667	0.600	10.90	1.09	0.917
D1A4	C (A4) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.22	0.41	2.439
	0.417	2.398	10.28	0.47	2.128
	0.550	1.818	10.33	0.52	1.923
	0.833	1.200	10.45	0.64	1.563
	1.667	0.600	10.56	0.75	1.333
D1A5	C (A5) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	9.97	0.16	6.250
	0.417	2.398	10.01	0.20	5.000
	0.550	1.818	10.07	0.26	3.846
	0.833	1.200	10.31	0.50	2.000
	1.667	0.600	10.42	0.61	1.639
D1A6	C (A6) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)

	0		9.81		
	0.333	3.003	11.40	1.59	0.629
	0.370	2.703	11.44	1.63	0.613
	0.417	2.398	11.47	1.66	0.602
	0.476	2.101	11.49	1.68	0.595
	0.550	1.818	11.52	1.71	0.585
D1A7	C (A7)	1/C	δ	$\Delta\delta$	1/ $\Delta\delta$
	(mol L ⁻¹)	(L mol ⁻¹)	(ppm)	(ppm)	(ppm ⁻¹)
	0		9.81		
	0.333	3.003	11.20	1.39	0.719
	0.417	2.398	11.31	1.50	0.671
	0.550	1.818	11.36	1.55	0.645
	0.833	1.200	11.40	1.59	0.629
D1A8	C (A8)	1/C	δ	$\Delta\delta$	1/ $\Delta\delta$
	(mol L ⁻¹)	(L mol ⁻¹)	(ppm)	(ppm)	(ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.79	0.98	1.020
	0.417	2.398	10.92	1.11	0.901
	0.550	1.818	11.01	1.20	0.833
	0.833	1.200	11.09	1.28	0.781
	1.667	0.600	11.18	1.37	0.729
D1A9	C (A9)	1/C	δ	$\Delta\delta$	1/ $\Delta\delta$
	(mol L ⁻¹)	(L mol ⁻¹)	(ppm)	(ppm)	(ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.36	0.55	1.818
	0.417	2.398	10.46	0.65	1.538
	0.550	1.818	10.56	0.75	1.333
	0.833	1.200	10.70	0.89	1.124
	1.667	0.600	10.72	0.91	1.099
D1A10	C (A10)	1/C	δ	$\Delta\delta$	1/ $\Delta\delta$
	(mol L ⁻¹)	(L mol ⁻¹)	(ppm)	(ppm)	(ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.07	0.26	3.846
	0.417	2.398	10.18	0.37	2.703
	0.550	1.818	10.22	0.41	2.439
	0.833	1.200	10.55	0.74	1.351
	1.667	0.600	10.98	1.17	0.855
D1A11	C (A11)	1/C	δ	$\Delta\delta$	1/ $\Delta\delta$
	(mol L ⁻¹)	(L mol ⁻¹)	(ppm)	(ppm)	(ppm ⁻¹)
	0		9.81		
	0.333	3.003	11.12	1.31	0.763
	0.370	2.703	11.14	1.33	0.752
	0.417	2.398	11.15	1.34	0.746
	0.476	2.101	11.16	1.35	0.741

	0.550	1.818	11.17	1.36	0.735
D1A12	C (A12) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.94	1.13	0.885
	0.417	2.398	11.02	1.21	0.826
	0.550	1.818	11.06	1.25	0.800
	0.833	1.200	11.09	1.28	0.781
D1A13	C (A13) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.45	0.64	1.563
	0.417	2.398	10.51	0.70	1.429
	0.550	1.818	10.56	0.75	1.333
	0.833	1.200	10.59	0.78	1.282
	1.667	0.600	10.77	0.96	1.042
D1A14	C (A14) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.24	0.43	2.326
	0.417	2.398	10.37	0.56	1.786
	0.550	1.818	10.41	0.60	1.667
	0.833	1.200	10.56	0.75	1.333
	1.667	0.600	10.71	0.90	1.111
D1A15	C (A15) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	11.01	1.20	0.833
	0.370	2.703	11.09	1.28	0.781
	0.417	2.398	11.14	1.33	0.752
	0.476	2.101	11.19	1.38	0.725
	0.550	1.818	11.21	1.40	0.714
D1A16	C (A16) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.91	1.10	0.909
	0.417	2.398	10.98	1.17	0.855
	0.550	1.818	11.11	1.30	0.769
	0.833	1.200	11.17	1.36	0.735
D1A17	C (A17) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.66	0.85	1.176

	0.417	2.398	10.79	0.98	1.020
	0.550	1.818	10.87	1.06	0.943
	0.833	1.200	10.91	1.10	0.909
	1.667	0.600	10.99	1.18	0.847
D1A18	C (A18) (mol L ⁻¹)	1/C (L mol ⁻¹)	δ (ppm)	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm ⁻¹)
	0		9.81		
	0.333	3.003	10.22	0.41	2.439
	0.417	2.398	10.35	0.54	1.852
	0.550	1.818	10.46	0.65	1.538
	0.833	1.200	10.57	0.76	1.316
	1.667	0.600	10.69	0.88	1.136

Table S6 Temperature dependence experiment of D1 with A1-A18. (stock [D1] = 1 mmol)

D1A1	[D1] (mol L ⁻¹)	[A1] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.82	2.381	-2.815
	1.667	0.417	303	3.300	10.59	2.360	-2.117
	1.667	0.417	308	3.247	10.36	2.338	-1.477
	1.667	0.417	313	3.195	10.13	2.316	-0.759
	1.667	0.417	318	3.145	9.89	2.292	0.417
	1.667	0.417	323	3.096	9.64	2.266	0.884
	1.667	0.417	328	3.049	9.44	2.245	1.444
D1A2	[D1] (mol L ⁻¹)	[A2] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	11.16	2.412	-4.778
	1.667	0.417	303	3.300	11.00	2.398	-3.545
	1.667	0.417	308	3.247	10.82	2.381	-2.815
	1.667	0.417	313	3.195	10.64	2.365	-2.259
	1.667	0.417	318	3.145	10.43	2.345	-1.673
	1.667	0.417	323	3.096	10.24	2.326	-1.122
	1.667	0.417	328	3.049	10.05	2.308	-0.451
D1A3	[D1] (mol L ⁻¹)	[A3] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.37	2.339	-1.505
	1.667	0.417	303	3.300	10.16	2.318	-0.863
	1.667	0.417	308	3.247	9.91	2.294	-0.022
	1.667	0.417	313	3.195	9.62	2.264	0.602
	1.667	0.417	318	3.145	9.37	2.238	1.025
	1.667	0.417	323	3.096	9.11	2.209	1.479
	1.667	0.417	328	3.049	8.84	2.179	2.224
D1A4	[D1] (mol L ⁻¹)	[A4] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.39	2.341	-1.562
	1.667	0.417	303	3.300	10.25	2.327	-1.153
	1.667	0.417	308	3.247	10.11	2.314	-0.686
	1.667	0.417	313	3.195	9.91	2.294	-0.266
	1.667	0.417	318	3.145	9.74	2.276	0.508
	1.667	0.417	323	3.096	9.54	2.255	0.895
	1.667	0.417	328	3.049	9.31	2.231	1.297
D1A5	[D1] (mol L ⁻¹)	[A5] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	9.76	2.278	-2.521
	1.667	0.417	303	3.300	9.60	2.262	-2.326
	1.667	0.417	308	3.247	9.40	2.241	-2.025
	1.667	0.417	313	3.195	9.24	2.219	-1.659

	1.667	0.417	318	3.145	9.04	2.202	-1.341
	1.667	0.417	323	3.096	8.82	2.177	-1.176
	1.667	0.417	328	3.049	8.62	2.154	-0.889
D1A6	[D1] (mol L ⁻¹)	[A6] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	11.08	2.405	-4.020
	1.667	0.417	303	3.300	10.94	2.392	-3.268
	1.667	0.417	308	3.247	10.78	2.378	-2.683
	1.667	0.417	313	3.195	10.62	2.363	-2.202
	1.667	0.417	318	3.145	10.47	2.349	-1.784
	1.667	0.417	323	3.096	10.31	2.333	-1.333
	1.667	0.417	328	3.049	10.13	2.316	-0.759
D1A7	[D1] (mol L ⁻¹)	[A7] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.80	2.380	-2.745
	1.667	0.417	303	3.300	10.70	2.370	-2.435
	1.667	0.417	308	3.247	10.52	2.353	-1.922
	1.667	0.417	313	3.195	10.36	2.338	-1.477
	1.667	0.417	318	3.145	10.19	2.321	-0.963
	1.667	0.417	323	3.096	10.00	2.303	-0.229
	1.667	0.417	328	3.049	9.83	2.285	0.977
D1A8	[D1] (mol L ⁻¹)	[A8] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.11	2.314	-0.686
	1.667	0.417	303	3.300	9.93	2.296	0.146
	1.667	0.417	308	3.247	9.70	2.272	0.878
	1.667	0.417	313	3.195	9.55	2.257	1.271
	1.667	0.417	318	3.145	9.37	2.238	1.452
	1.667	0.417	323	3.096	9.18	2.217	2.186
	1.667	0.417	328	3.049	8.94	2.191	2.212
D1A9	[D1] (mol L ⁻¹)	[A9] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.59	2.360	-2.117
	1.667	0.417	303	3.300	10.42	2.344	-1.698
	1.667	0.417	308	3.247	10.26	2.328	-1.145
	1.667	0.417	313	3.195	10.07	2.309	-1.777
	1.667	0.417	318	3.145	9.93	2.296	-2.219
	1.667	0.417	323	3.096	9.71	2.273	-2.442
	1.667	0.417	328	3.049	9.52	2.253	-2.953
D1A10	[D1] (mol L ⁻¹)	[A10] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	9.98	2.301	-0.131
	1.667	0.417	303	3.300	9.86	2.288	0.665
	1.667	0.417	308	3.247	9.67	2.269	0.779

	1.667	0.417	313	3.195	9.50	2.251	0.899
	1.667	0.417	318	3.145	9.37	2.237	1.290
	1.667	0.417	323	3.096	9.13	2.212	1.667
	1.667	0.417	328	3.049	8.89	2.185	1.923
D1A11	[D1] (mol L ⁻¹)	[A11] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.97	2.395	-3.401
	1.667	0.417	303	3.300	10.80	2.379	-2.748
	1.667	0.417	308	3.247	10.61	2.362	-2.174
	1.667	0.417	313	3.195	10.42	2.343	-1.646
	1.667	0.417	318	3.145	10.22	2.324	-1.060
	1.667	0.417	323	3.096	10.04	2.306	-0.409
	1.667	0.417	328	3.049	9.83	2.285	0.977
D1A12	[D1] (mol L ⁻¹)	[A12] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.66	2.366	-2.317
	1.667	0.417	303	3.300	10.48	2.349	-1.812
	1.667	0.417	308	3.247	10.26	2.328	-1.184
	1.667	0.417	313	3.195	10.04	2.306	-0.409
	1.667	0.417	318	3.145	9.81	2.283	-0.064
	1.667	0.417	323	3.096	9.58	2.259	0.244
	1.667	0.417	328	3.049	9.36	2.236	0.717
D1A13	[D1] (mol L ⁻¹)	[A13] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.21	2.323	-1.028
	1.667	0.417	303	3.300	9.99	2.302	-0.181
	1.667	0.417	308	3.247	9.73	2.275	-0.056
	1.667	0.417	313	3.195	9.48	2.249	0.254
	1.667	0.417	318	3.145	9.20	2.219	0.931
	1.667	0.417	323	3.096	8.95	2.192	1.071
	1.667	0.417	328	3.049	8.69	2.193	1.716
D1A14	[D1] (mol L ⁻¹)	[A14] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.11	2.314	-0.686
	1.667	0.417	303	3.300	9.95	2.293	0.029
	1.667	0.417	308	3.247	9.74	2.276	0.107
	1.667	0.417	313	3.195	9.57	2.259	0.309
	1.667	0.417	318	3.145	9.44	2.245	0.540
	1.667	0.417	323	3.096	9.20	2.219	0.931
	1.667	0.417	328	3.049	8.99	2.196	1.066
D1A15	[D1] (mol L ⁻¹)	[A15] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	11.08	2.405	-4.020
	1.667	0.417	303	3.300	10.95	2.393	-3.311

	1.667	0.417	308	3.247	10.79	2.379	-2.715
	1.667	0.417	313	3.195	10.64	2.365	-2.259
	1.667	0.417	318	3.145	10.48	2.349	-1.812
	1.667	0.417	323	3.096	10.31	2.333	-1.333
	1.667	0.417	328	3.049	10.16	2.318	-0.863
D1A16	[D1] (mol L ⁻¹)	[A16] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.96	2.394	-3.355
	1.667	0.417	303	3.300	10.80	2.379	-2.748
	1.667	0.417	308	3.247	10.64	2.364	-2.259
	1.667	0.417	313	3.195	10.49	2.392	-1.839
	1.667	0.417	318	3.145	10.28	2.330	-1.244
	1.667	0.417	323	3.096	10.10	2.312	-0.649
	1.667	0.417	328	3.049	9.92	2.295	-0.479
D1A17	[D1] (mol L ⁻¹)	[A17] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.66	2.366	-2.317
	1.667	0.417	303	3.300	10.50	2.351	-1.867
	1.667	0.417	308	3.247	10.24	2.326	-1.409
	1.667	0.417	313	3.195	10.13	2.316	-1.081
	1.667	0.417	318	3.145	9.92	2.295	-0.703
	1.667	0.417	323	3.096	9.72	2.274	-0.291
	1.667	0.417	328	3.049	9.49	2.250	-0.130
D1A18	[D1] (mol L ⁻¹)	[A18] (mol L ⁻¹)	<i>T</i> (K)	1/ <i>T</i> ×1000 (K ⁻¹)	δ (ppm)	ln δ	σ_δ
	1.667	0.417	298	3.356	10.35	2.337	-1.448
	1.667	0.417	303	3.300	10.17	2.319	-0.897
	1.667	0.417	308	3.247	10.08	2.311	-0.572
	1.667	0.417	313	3.195	9.90	2.293	-0.395
	1.667	0.417	318	3.145	9.70	2.272	-0.199
	1.667	0.417	323	3.096	9.51	2.252	0.074
	1.667	0.417	328	3.049	9.32	2.232	0.271

Table S7 The element content results of the regenerated formate cellulose.

Elements	C	O	Cl	Zn	Total
Wt%	47.58	52.33	0.02	0.07	100
At%	54.80	45.16	0.01	0.04	100

Table S8 The cost of raw materials of solvent consumed for dissolving one gram of cellulose with different solvents and the energy consumption during the dissolution process^[6].

Chemical agent	Price (\$/kg or \$/L)	Dosage (g or mL)	Materials cost (\$/g)	Temperature (°C)	Time (h)	Energy cost (\$/g)
BMIMCl	719.75	8.33	5.997	100	2	0.397
NMMO	689.13	7.14	4.922	130	2	0.397
LiCl	1223.58	1.50	1.835	150	6	1.192
DMAc	13.78	30.00	0.414	-12	12	0.109
NaOH	11.94	1.40	0.017	RT	2	0
Urea	18.99	2.40	0.045			
ZnCl ₂	48.68	2.11	0.103			
FA	15.20	2.86	0.043			

Materials purchased from the Kermel Chemical Reagent Co., Ltd.

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