

## Electronic Supplementary Information

### Homogeneous Cyanoethylation of Cellulose with Acrylonitrile in CO<sub>2</sub>

#### Switchable Solvent

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## **Experimental Section**

### **Materials**

Corncob cellulose (DP=1440) from Shengquan New Material Company (Shandong, China) was vacuum dried at 80 °C for 24 h and kept in a desiccator for further use. Dimethyl sulfoxide (DMSO, >99.8%), Acrylonitrile (AN, >99%), methanol (>99.5%), and 1,8-diazabicyclo [5.4.0]under-7-ene (DBU) were purchased from Aladdin Reagents Co.Ltd (Shanghai, China). All chemicals were used as received without further purification.

### **Dissolution of Cellulose with CO<sub>2</sub> Switchable Solvent**

Dissolution of cellulose was performed with the CO<sub>2</sub> switchable solvent to prepare homogeneous cellulose solution according to our previous study.<sup>1,2</sup> Typically, corn cob cellulose (4.72 g, 29.1 mmol), DBU (13.28 g, 87.3 mmol), and DMSO (100.00 g, 90.9 mL) were added to a 250 mL stainless steel reactor equipped with a gas inlet and an outlet. The molar ratio of DBU to the anhydroglucose unit (AGU) was 3:1. The reactor was then closed and kept at 55 °C and atmospheric pressure with magnetic stirring, and CO<sub>2</sub> was continuous introduced through the gas inlet for 2 h. A transparent and yellowish homogeneous solution with cellulose concentration of 4 wt% was obtained.

### **Homogeneous Cyanoethylation of Cellulose in CO<sub>2</sub> Switchable Solvent**

Typically, a pre-determined amount of AN was added dropwise into 20.0 g cellulose solution prepared above, and the mixture was mechanically stirred at certain temperature for a desired amount of time. By changing the reaction conditions such as temperature, time, and molar ratio of AN and DBU to AGU, twenty-six CEC samples were prepared. After the reaction was completed, the mixture was precipitated with methanol and then filtered, and then washed several times to remove DMSO, DBU, and

the unreacted AN. The CEC final product was obtained as white powder after dried under reduced pressure at 60 °C for 24 h.

### **Reaction of AN with DBU**

A mixture of AN and DBU (molar ratio=1:1) was mechanically stirred at 60 °C for 8 h. After the reaction was completed, the mixture was precipitated with methanol and then filtered, and then washed several times with methanol to remove DBU and the unreacted AN. The reaction product was obtained as yellow powder after dried under reduced pressure at 60 °C for 24 h.

### **Separating and Analyzing of the Possible By-product**

After dissolution of cellulose, the cellulose solution was precipitated with methanol and then filtered to remove DMSO, DBU, and the unreacted AN. The filtrate was subjected to rotary evaporation under vacuum at 90 °C to remove methanol and DMSO. The remaining small amount of liquid was kept still over night to precipitate sediment which was filtered and dried under reduced pressure at 60 °C for 24 h to give yellow-brownish solid residue.

### **Characterization**

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra of CEC samples were recorded on a Bruker AVANCE III 400 MHz NMR apparatus, by using DMSO-*d*<sub>6</sub> as the solvent. <sup>13</sup>C NMR spectra of CEC samples were recorded on a Bruker AVANCE III 600 MHz NMR apparatus, by using DMSO-*d*<sub>6</sub> as the solvent.

Fourier transform infrared (FT-IR) spectroscopy was recorded using Nicolet 6700 instrument. Samples were tested with KBr pellet method. Each spectrum was recorded in the range of 400-4000 cm<sup>-1</sup> of 0.9 cm<sup>-1</sup> with 32 scans.

Nitrogen content (N%) of CEC samples was determined by an elemental analyzer (CHN) in accordance with nimTE-40 operating document 15-2007 operating procedure

for organic Elemental Analyzer. The degree of substitution (*DS*) of the cyanoethyl group can be calculated from N% according to the following formula  $DS = (162 \times N\%) / (1400 - 53 \times N\%)$ .

X-ray diffraction (XRD) measurements were performed with D8 ADVANCE X-ray Diffractometer, and the diffraction intensity was measured in a range of  $2\theta = 5-40^\circ$ .

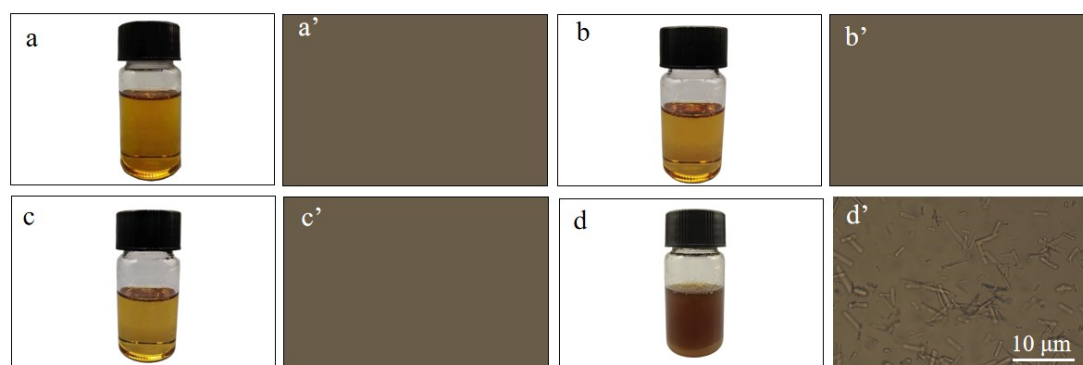
Thermogravimetric analysis (TGA) was carried on a Diamond TG/DTA thermogravimetric analyzer with a heating rate of  $10^\circ\text{C} \cdot \text{min}^{-1}$  from 25 to  $810^\circ\text{C}$  under nitrogen atmosphere.

Gel permeation chromatographic (GPC) measurement was carried out with HLC8320 TSKgel SuperAWM-H column, DMF was used as the eluent with a flow rate of  $0.6 \text{ mL min}^{-1}$  at room temperature .

The solubility of the CEC samples in different solvents was measured at room temperature with the concentration of about 0.5 M.

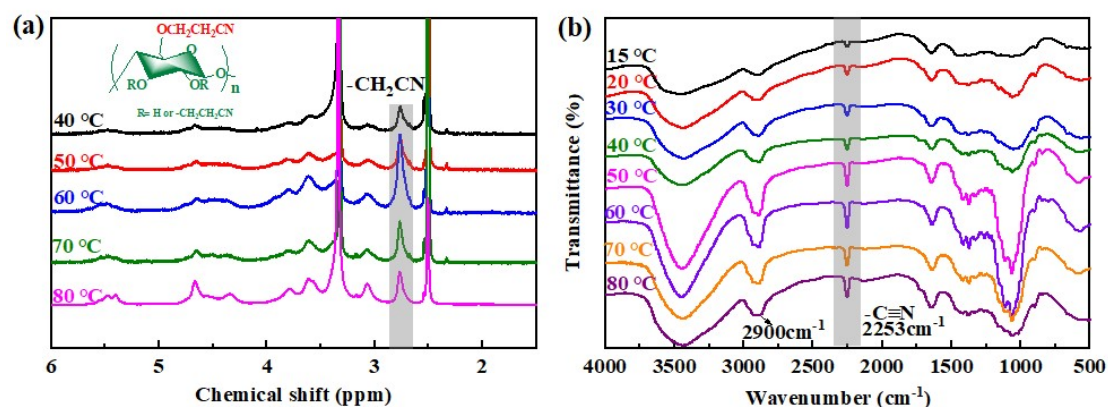
Polymer samples with controlled low molecular weight were analysed by Time of Flight Mass Spectrometer (LC-Q-TOF), which carried out with Triple TOF-4600 in linear, positive ESI ion at 55 KV accelerating voltage.

A polarized optical microscope (POM, Olympus BX51) was used to observe the dissolution state of the cellulose solution. A drop of the cellulose solution was placed on a glass slide, and the presence of crystals in the dope was observed.

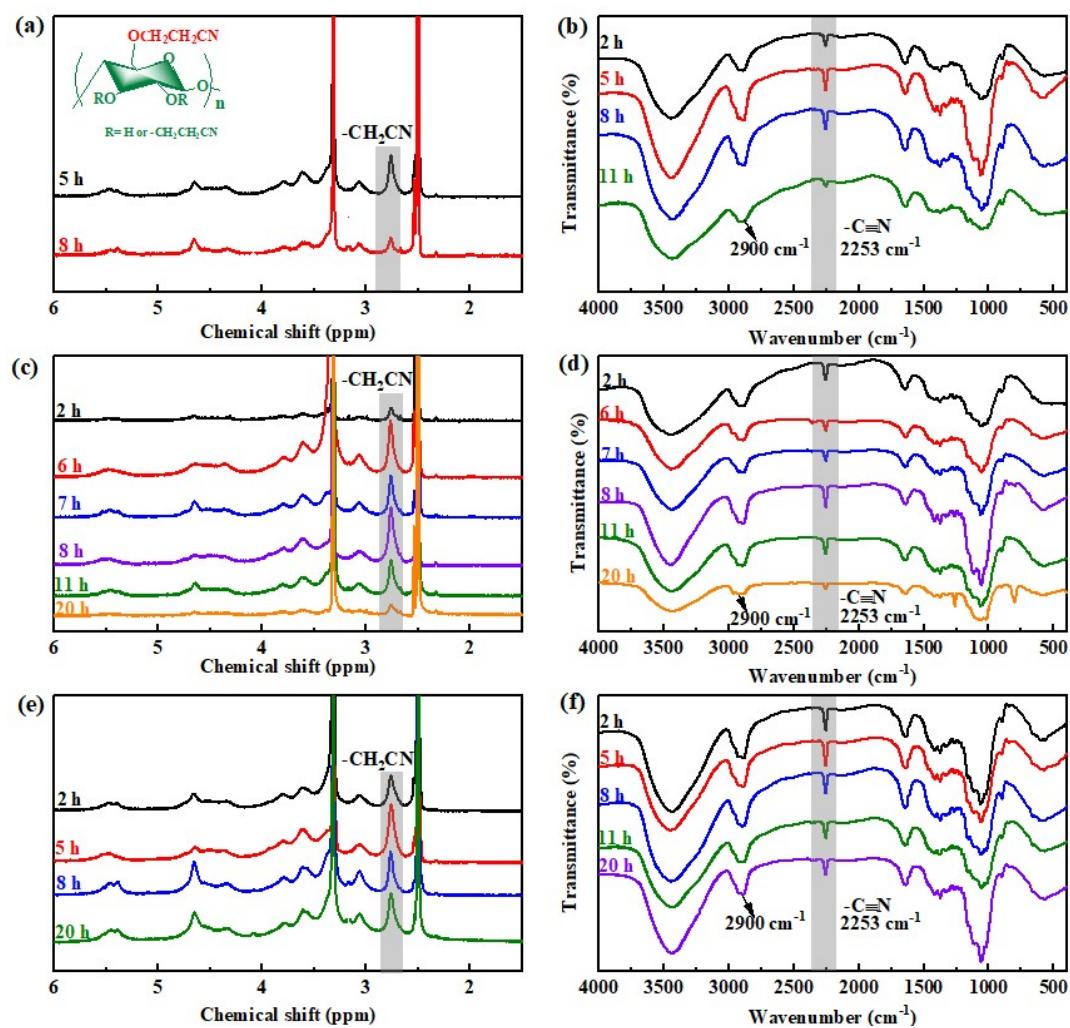


**Figure S1.** Cellulose solutions (a-d) and their POM images (a'-d') obtained by using

different molar ratio of DBU:AGU: (a, a') 2.5:1, (b, b') 3:1, (c, c') 3.5:1 and (d, d') 4:1.



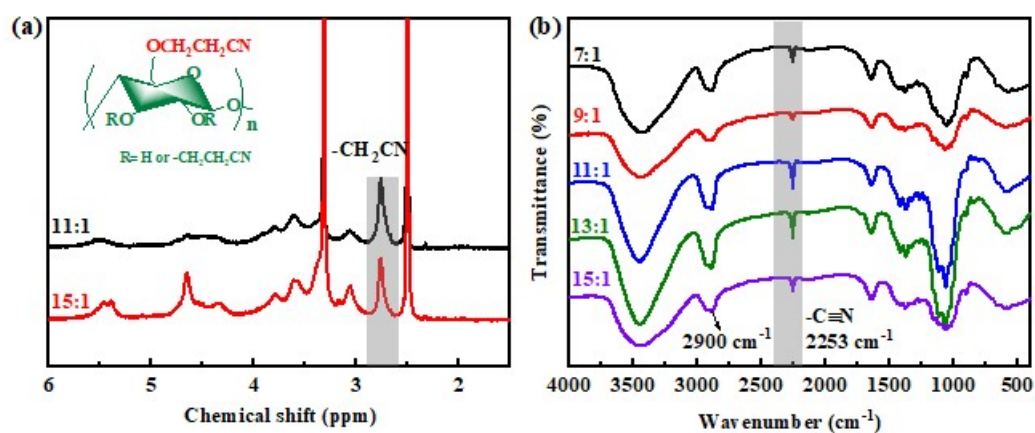
**Figure S2.** (a) <sup>1</sup>H NMR spectrum and (b) FT-IR spectrum of CEC sample prepared at different temperatures. Reaction conditions: 4 wt% cellulose solution, DBU:AGU=3:1, AN:AGU=11:1, 8 h.



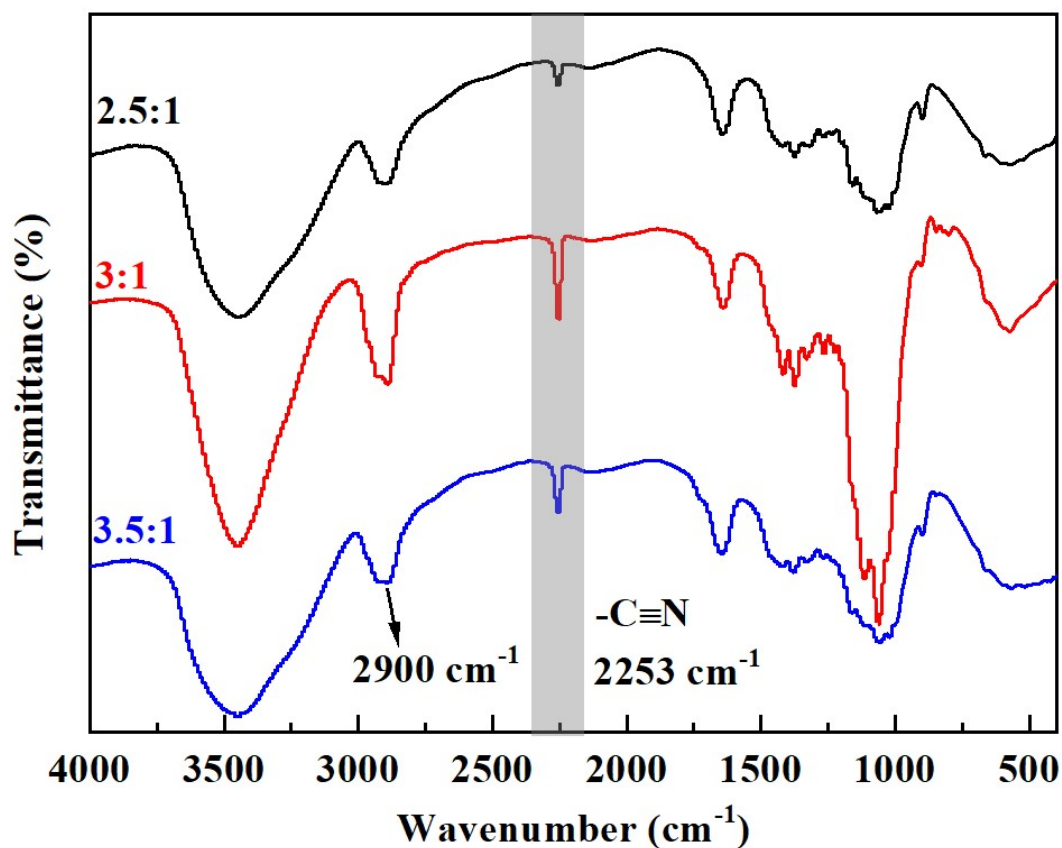
**Figure S3.**  $^1\text{H}$  NMR and FT-IR spectra of CEC samples prepared with different reaction time with different molar ratio of AN:AGU: (a, b) 7:1, (c, d) 11:1, and (e, f) 15:1. Reaction conditions: 4 wt% cellulose solution, DBU:AGU=3:1, 60 °C.

**Table S1.** Results for the cyanoethylation of cellulose in CO<sub>2</sub> switchable solvent with different reaction time under different molar ratio of AN:AGU.

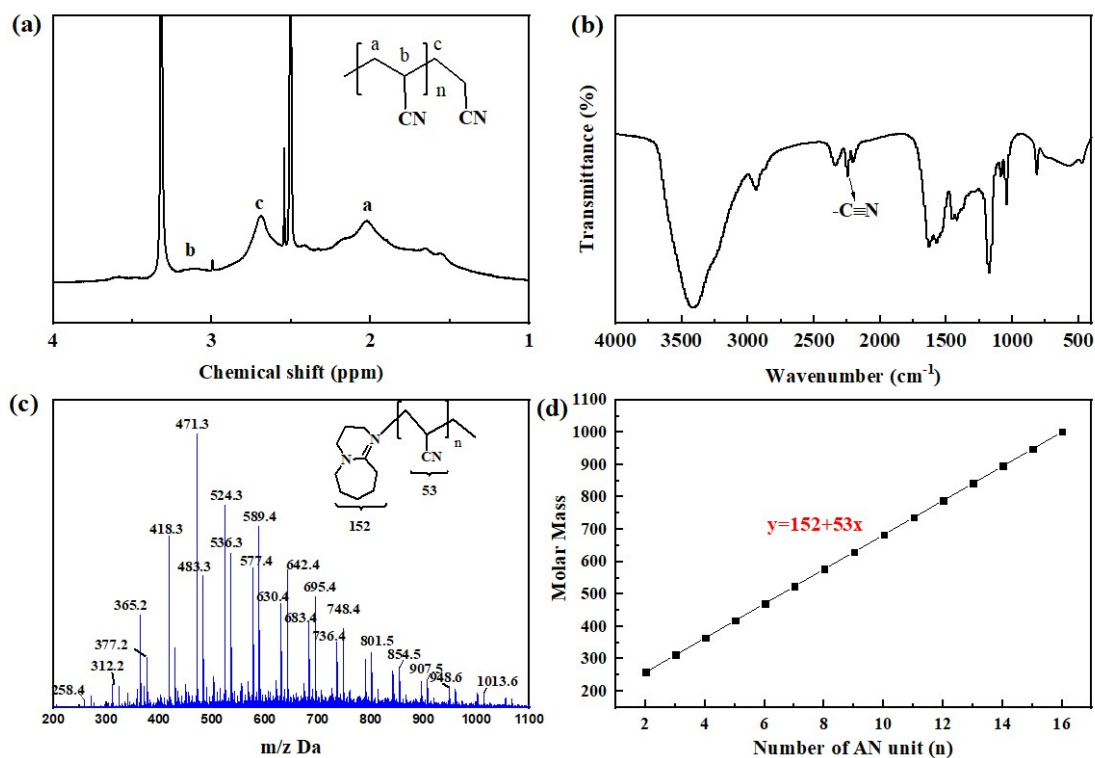
Sample	$T$ (°C)	$t$ (h)	Molar ratio		N content (%)	$DS$		Solubility	
			AN:AGU	DBU:AGU		Elemental analysis	NMR	0.5 M NaOH	DMSO
CEC-20	60	2	7:1	3:1	2.83±0.02	0.37±0.01	/	++	-
CEC-21	60	5	7:1	3:1	5.08±0.02	0.73±0.02	0.70	-	++
CEC-22	60	11	7:1	3:1	1.05±0.01	0.13±0.01	/	++	-
CEC-23	60	2	15:1	3:1	4.59±0.02	0.64±0.01	0.59	-	+
CEC-24	60	5	15:1	3:1	6.37±0.02	0.97±0.02	0.82	-	++
CEC-25	60	11	15:1	3:1	3.78±0.02	0.50±0.01	0.45	+	+
CEC-26	60	20	15:1	3:1	3.61±0.07	0.48±0.01	0.69	-	++



**Figure S4.** (a) <sup>1</sup>H NMR spectrum and (b) FT-IR spectrum of CEC sample at different feeding molar ratio of AN:AGU. Reaction conditions: 4 wt% cellulose solution, DBU:AGU=3:1, 60 °C, 8 h.

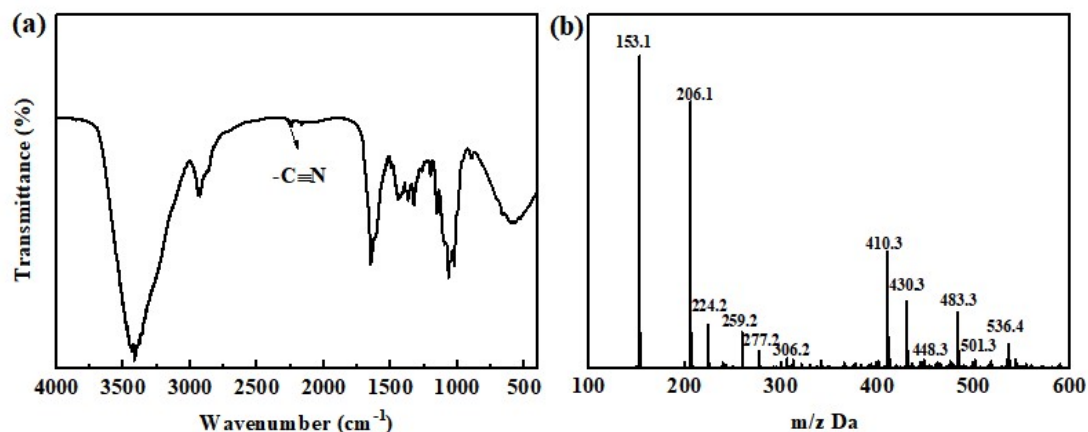


**Figure S5.** FT-IR spectrum of CEC sample at different feeding molar ratio of AN to AGU. Reaction conditions: 4 wt% cellulose solution, AN:AGU=11:1, 60 °C, 8 h.





**Figure S6.** (a)  $^1\text{H}$  NMR spectrum, (b) FT-IR spectrum, (c) LC-Q-TOF of product obtained by reacting AN with DBU, and (d) the calculated number of AN unit in the product corresponding to the molar mass detected by LC-Q-TOF.



**Figure S7.** (a) FT-IR and (b) LC-Q-TOF spectra of solid residue obtained by rotary evaporation of the filtrate after sample separation.

**Table S2.** Comparison of the *DS* range of the solubility of CEC samples in NaOH solution and DMSO obtained in  $\text{CO}_2$  switchable solvent and NaOH/Urea/ $\text{H}_2\text{O}$  system.

Dissolution Systems	$\text{CO}_2$ Switchable Solvent	NaOH/Urea/ $\text{H}_2\text{O}$ <sup>3</sup>
Soluble in NaOH solution	<i>DS</i> : 0.12-0.46	<i>DS</i> : 0.26-0.54
Soluble in both NaOH solution and DMSO	<i>DS</i> : 0.46-0.50	<i>DS</i> : 0.54-0.69
Soluble in DMSO	<i>DS</i> : 0.50-1.03	<i>DS</i> : 0.69-1.93

## References

1. S. Lu, J. Li, F. Liu, M. Chen, H. Na and J. Zhu, *Polymer (Guildf)*., 2021, **229**, 124020.
2. J. Li, S. Lu, F. Liu, Q. Qiao, H. Na and J. Zhu, *ACS Sustain. Chem. Eng.*, 2021, **9**, 4744–4754.
3. J. Zhou, Q. Li, Y. Song, L. Zhang and X. Lin, *Polym. Chem.*, 2010, **1**, 1662 – 1668.