Electronic Supplementary Information

Cellulosic Poly(ionic liquid)s: Synthesis, Characterization and its Application in the Cycloaddition of CO_2 to Epoxides

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1.0 Experimental Details

1.1 Materials, chemicals and instruments

Microcrystalline cellulose (MCC) with a degree of polymerization (DP) of 240 was obtained from Aladdin Commerce Reagent Co., Ltd. and dried at 60 °C for 24 h in vacuum oven before use. Thionyl chloride was obtained from Tianjin Damao chemical reagent Factory. N-methylimidazole was purchased from TCI and distilled with CaH_2. CO_2 with a purity of >99.999% was supplied from Beijing Bei Temperature Gas Factory. Propylene oxide was supplied by Sinopharm Chemical Reagent Co., Ltd. Other reagent were supplied by local chemical company and used as received.

^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 500 MHz. Chemical shifts (δ) were reported in parts per million (ppm). Nitrogen contents were measured with an elemental analyzer (various ELIII, Elementar, Germany). Fourier transform infrared spectroscopy (FT-IR) measurements were recorded on Tensor 27 in the range of 400-4000 cm^{-1}.

Thermo gravimetric analyses were acquired under nitrogen with a TGA-DSC STA 449F-3 instruments. About 5 mg of sample was heated at 10 °C/min from 40 to 650 °C. Differential scanning calorimetry (DSC) experiments were performed on a DSC 204 HP instruments. The samples (5-10 mg) were enclosed in aluminium pan and placed in the heating cell with an empty pan as reference. All samples were heated under nitrogen flow (20 mL/min) from -100 °C to 150 °C at a heating rate of 10 °C/min.

1.2 Synthesis of 6-chloro-6-deoxycellulose (CDC).

The 6-chloro-6-deoxycellulose (CDC) was prepared according to the literature[1]. Microcrystalline cellulose powder (10 g) was suspended in dimethylformamide (200 mL) and heated to 80 °C under mechanical stirring. Thionyl chloride (35 mL) was gradually added to the suspension. After the addition was complete, the reaction was continued for 2.5 h at 90 °C. The viscous solution was cooled to room temperature and poured into ice water (500 mL) with agitation. The precipitated CDC was filtered, washed with water and treated with dilute ammonium hydroxide. Furthermore, the CDC was washed thoroughly with water to bring the pH to neutral and then

lyophilized. The degree of chlorine substitution is 0.89 determined by oxygen flask combustion method[2].

1.3 Synthesis of cellulose anchored 1-methyl-imidazolium chloride ([Cellmim][Cl])

A sample of CDC (0.5 g) was reacted with N-methylimidazole (5 mL) at 100 °C with mechanical stirring for 24 h. The solution was poured into methanol and the precipitate was washed thoroughly with methanol then dried in vacuum at 60 °C for 24 h to obtain [Cellmim][Cl]. The degree of substitution (DS) was determined by nitrogen content from elemental analysis using the flowing equation (1)

$$DS = \frac{N\% \times 178.5}{1400 \times \mathrm{n} - N\% \times \mathrm{M}} \quad (1)$$

Where n is the number of nitrogen in 1-methylimidazole. M is the molecular weight of 1-methylimidazole. The cellulose anchored 1-methyl-imidazolium bromide moieties ([Cellmim][Br]) and cellulose anchored 1-methyl-imidazolium iodine moieties ([Cellmim][I]) were prepared through ionic exchange of [Cellmim][Cl] with saturated water solution of NaBr and NaI respectively.

1.4 Typical procedure for the cycloaddition of CO_2 to epoxides.

In a typical procedure, $[Cellmim][Cl]_{DS=0.64}$ (300 mg), propylene oxide (20 mmol) were added into a 25 mL stainless steel autoclave equipped with a magnetic stirrer. Then, CO_2 was charged in the autoclave and adjusted to 2 MPa. The reaction was carried out at specified temperature for a desired period of time. After the reaction, the autoclave was cooled to 0 °C and the excess CO_2 was slowly vented. The catalyst was separated by filtration and washed with ethyl acetate. The product was purified by distillation and identified by NMR spectra. The yields were calculated according to the equation below:

$$\text{Yield } (\%) = (m_{cyclic\ carbonate}/Mw_{\ cyclic\ carbonate})/M_{related\ epoxide}) \times 100\ \%$$

Where $m_{cyclic\ carbonate}$ is the mass of separated and purified cyclic carbonate, and $Mw_{cyclic\ carbonate}$ is the molecular weight of the cyclic carbonate, and $M_{epoxide}$ is the mole number of the corresponding epoxide used for the reaction.

4-methyl-1, 3-dioxolan-2-one: ^{1}H NMR (500 MHz, $CDCl_3$) δ =1.46 (d, J = 5.7 Hz, 3H), 4.00 (t, J = 7.6 Hz, 1H), 4.53 (t, J = 7.9 Hz, 1H), 4.83 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ= 19.52, 70.81, 73.68, 155.16 ppm (C=O).

4-chloromethyl-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.03-4.98 (m, 1H), 4.63-4.59 (t, J = 8.6 Hz, 1H), 4.44-4.40 (q, J = 4.9 Hz, 1H), 3.84-3.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 74.4, 66.9, 43.9.

4-bromomethyl-1,3-dioxolan-2-one, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.98-4.92 (m, 1H), 4.61-4.57 (q, J = 5.7 Hz, 1 H), 4.37-4.33 (q, J = 4.9 Hz, 1H), 3.58-2.57 (d, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2, 74.0, 68.1, 31.3.

4-phenoxymethyl-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.29 (q, *J* = 5.3 Hz, 2H), 7.03-7.00 (t, *J* = 7.4Hz, 1H), 5.05-4.99 (m, 1H), 4.63-4.51 (m, 2H), 4.23-4.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 154.7, 129.7, 122.0, 114.6, 74.2, 66.9, 66.2.

4-phenyl-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.35 (m, 5H), 5.70-5.66 (t, *J* = 5.3 Hz, 1H), 4.82-4.78 (t, *J* = 8.4 Hz, 1H), 4.36-4.32 (t, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 135.8, 129.8, 129.3, 125.9, 78.0, 71.2.

2.0 Supplemental Tables and Figures

Table S1. The controllability of DS and solubility of [Cellmim][Cl] in conventional solvents

Entry	Solvent	T	t	DS	Solubility[a]	
		°C	h		H_2O	DMSO
1	none	80	24	0.14	±	+
2	none	90	24	0.37	+	+
3	none	100	24	0.56	+	±
4	none	100	48	0.64	+	±
5	DMSO	90	72	0.35	+	+
6	DMSO	100	24	0.42	+	±
7	AmimCl	90	24	0.30	+	+

a:± stands for swollen + stands for soluble

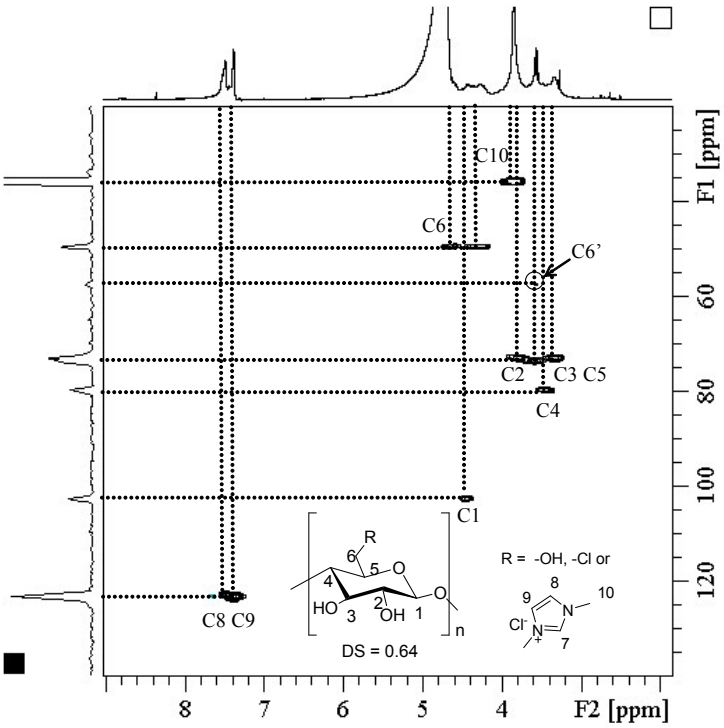

Figure S1. HSQC spectrum of [Cellmim][Cl]$_{DS=0.64}$ (400 MHz, D_2O)

Table S2. ^{1}H NMR and ^{13}C NMR resonances of [Cellmim][Cl]$_{DS=0.64}$ in D_2O from HSQC.

Resonance assignment	^{1}H ppm	^{13}C ppm
C1	4.44	102.3
C2	4.30	49.5
C3	3.60	73.7
C4	3.45	79.8
C5	3.35	73.1
C6	4.30, 4.67	49.5
C6’	3.58	57.5
C8	7.48	122.9
C9	7.37	123.4
C10	3.85	35.9

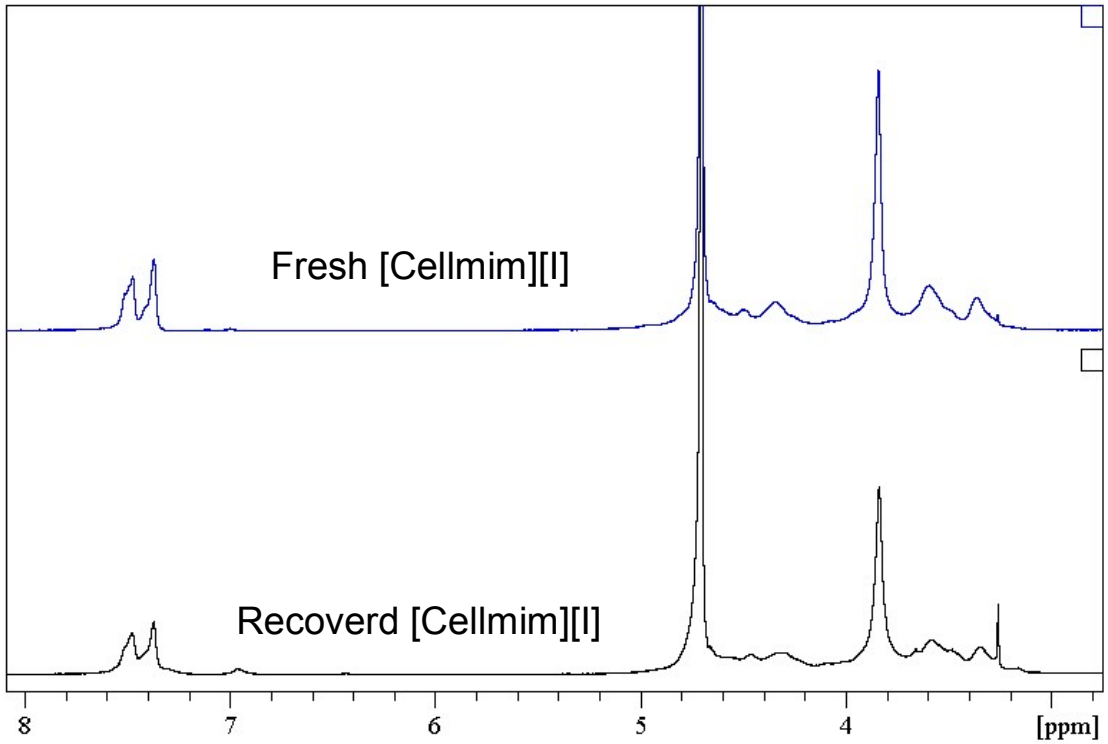

Figure S2. ^{1}H NMR spectra of fresh and recovered [Cellmim][I] (400 MHz, D_2O)

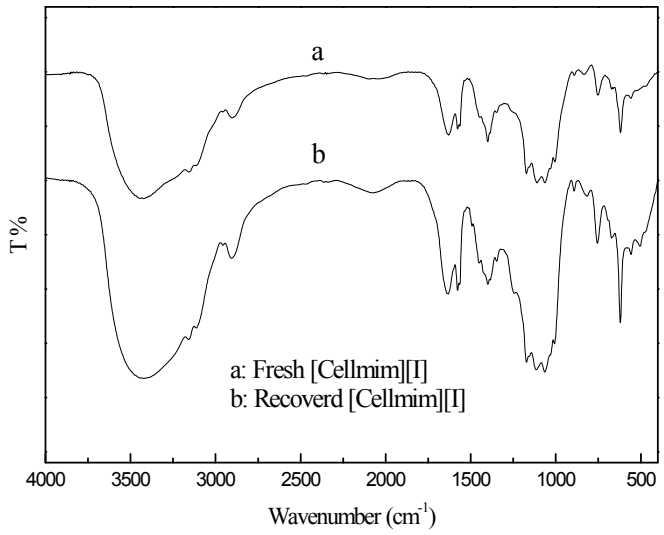

Figure S3. FTIR spectra of fresh and recovered [Cellmim][I].

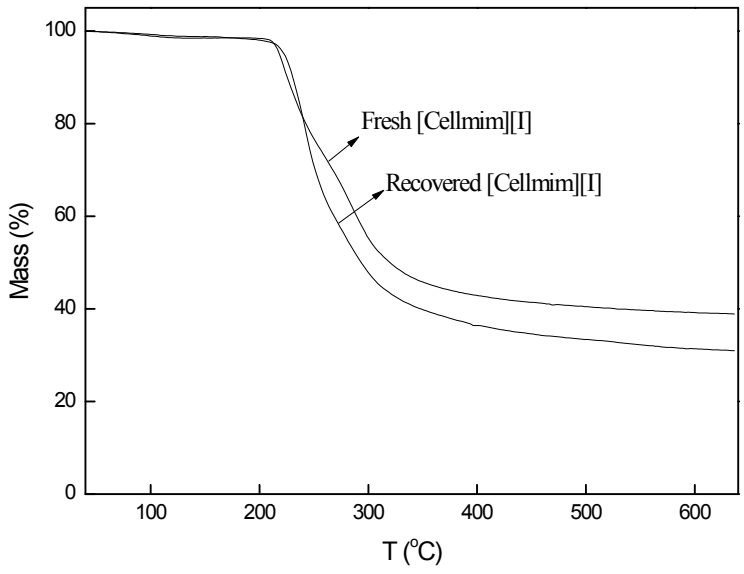

Figure S4. TGA analysis of fresh and recovered [Cellmim][I].

3.0 References

1. T. Tashiro and Y. Shimura, *J. Appl. Polym. Sci.*, 1982. **27**(2), 747-756.
2. A.M.G., MacDonald, *Analyst*, 1961. **86**(1018), 3-12.