SUPPORTING INFORMATION

Solid-state NMR reveals a structural deviation from cellulose Iβ in bacterial cellulose

Darren H. Brouwer* and Janelle G. Mikolajewski

Department of Chemistry, Redeemer University, Ancaster ON, Canada, L8P 2R5

dbrouwer@redeemer.ca

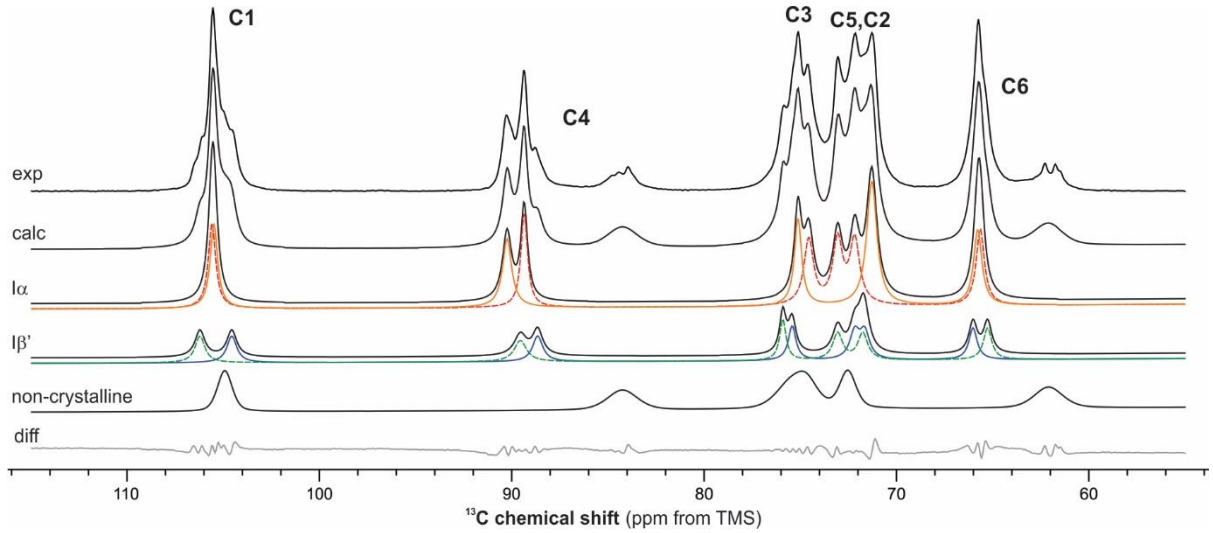

Fig. S1 Experimental 1D ^{13}C CP MAS NMR spectrum of 25% uniformly ^{13}C-enriched bacterial cellulose, along with the best-fit calculated model spectrum which is composed of contributions from cellulose Iα, cellulose Iβ', and non-crystalline cellulose. See Table S1 below for fitting parameters

Table S1 Model spectrum parameters for the calculated ^{13}C CP MAS NMR spectrum of 25% uniformly ^{13}C-enriched bacterial cellulose displayed above in Fig. S1

	Chemical shift (ppm)	Peak width (ppm)	Peak area (%)		Chemical shift (ppm)	Peak width (ppm)	Peak area (%)
Glucose unit 1 of **Cellulose Iα**				**Glucose unit 2** of **Cellulose Iα**			
C1(α1)	105.58	0.46	4.63	C1(α2)	105.48	0.46	4.63
C2(α1)	72.17	0.61	4.63	C2(α2)	71.23	0.61	4.63
C3(α1)	74.56	0.60	4.63	C3(α2)	75.12	0.45	4.63
C4(α1)	89.35	0.42	4.63	C4(α2)	90.24	0.57	4.63
C5(α1)	73.05	0.61	4.63	C5(α2)	71.33	0.61	4.63
C6(α1)	65.64	0.52	4.63	C6(α2)	65.77	0.52	4.63
Glucose unit 1 of **Cellulose Iβ'**				**Glucose unit 2** of **Cellulose Iβ'**			
C1(β'1)	104.55	0.62	1.93	C1(β'2)	106.21	0.62	1.93
C2(β'1)	71.65	0.61	1.93	C2(β'2)	71.75	0.61	1.93
C3(β'1)	75.42	0.48	1.93	C3(β'2)	75.91	0.40	1.93
C4(β'1)	88.65	0.64	1.93	C4(β'2)	89.55	0.77	1.93
C5(β'1)	72.17	0.61	1.93	C5(β'2)	73.06	0.61	1.93
C6(β'1)	66.02	0.52	1.93	C6(β'2)	65.26	0.52	1.93
Non-crystalline cellulose							
C1(nc)	104.91	0.91	3.54				
C2(nc)	72.53	1.00	3.54				
C3(nc)	75.61	1.74	3.54				
C4(nc)	84.24	1.85	3.54				
C5(nc)	74.70	1.44	3.54				
C6(nc)	62.09	1.77	3.54				

*The peaks for cellulose Iα and Iβ' were 100% Lorentzian, while peaks for non-crystalline cellulose were 50% Lorentzian/50% Gaussian.

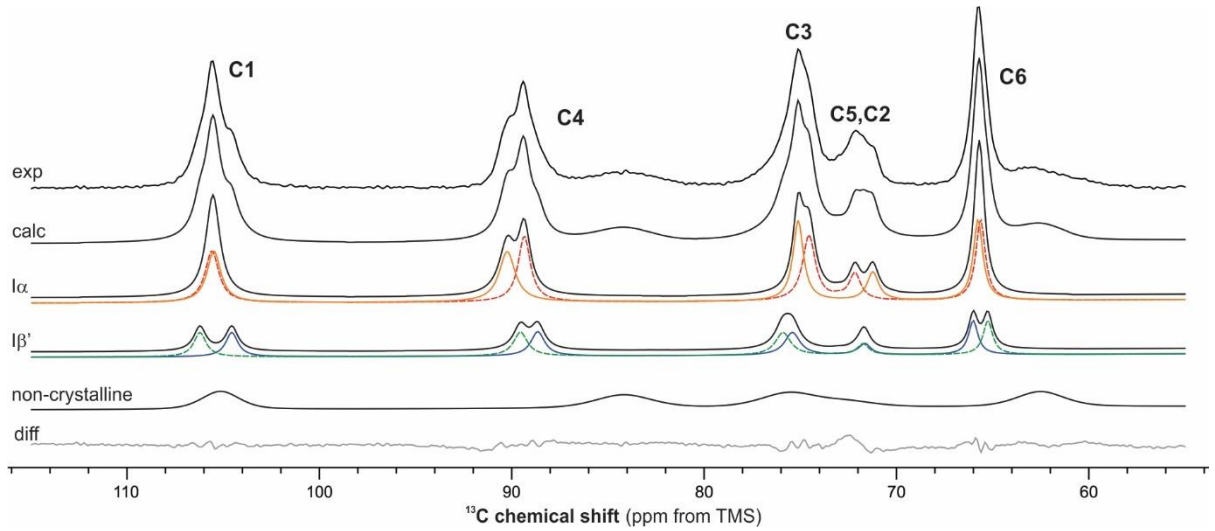

Fig. S2 Experimental 1D ^{13}C CP MAS NMR spectrum of bacterial cellulose ^{13}C-enriched at C1, C3, C4, and C6, along with the best-fit calculated model spectrum which is composed of contributions from cellulose Iα, cellulose Iβ', and non-crystalline cellulose. See Table S2 below for fitting parameters

Table S2 Model spectrum parameters for the calculated ^{13}C CP MAS NMR spectrum of bacterial cellulose ^{13}C-enriched at C1, C3, C4 and C6 displayed above in Fig. S2

	Chemical shift (ppm)	Peak width (ppm)	Peak area (%)		Chemical shift (ppm)	Peak width (ppm)	Peak area (%)
Glucose unit 1 of **Cellulose Iα**				**Glucose unit 2** of **Cellulose Iα**			
C1(α1)	105.58	0.86	5.74	C1(α2)	105.48	0.86	5.74
C2(α1)	72.17	0.72	2.47	C2(α2)	71.23	0.72	2.47
C3(α1)	74.56	0.79	6.71	C3(α2)	75.12	0.65	6.71
C4(α1)	89.35	0.76	6.49	C4(α2)	90.24	0.99	6.49
C5(α1)	73.05	0.72	0.20	C5(α2)	71.33	0.72	0.20
C6(α1)	65.64	0.59	6.17	C6(α2)	65.77	0.59	6.17
Glucose unit 1 of **Cellulose Iβ'**				**Glucose unit 2** of **Cellulose Iβ'**			
C1(β'1)	104.55	0.76	2.40	C1(β'2)	106.21	0.76	2.40
C2(β'1)	71.65	0.72	1.03	C2(β'2)	71.75	0.72	1.03
C3(β'1)	75.42	0.96	2.81	C3(β'2)	75.91	0.96	2.81
C4(β'1)	88.65	0.86	2.71	C4(β'2)	89.55	0.88	2.71
C5(β'1)	72.17	0.72	0.08	C5(β'2)	73.05	0.72	0.08
C6(β'1)	66.02	0.59	2.58	C6(β'2)	65.26	0.59	2.58
Non-crystalline cellulose							
C1(nc)	105.13	2.33	4.38				
C2(nc)	72.53	3.47	1.88				
C3(nc)	75.62	3.47	5.12				
C4(nc)	84.18	3.55	4.95				
C5(nc)	74.70	3.47	0.15				
C6(nc)	62.53	2.97	4.71				

* The peaks for cellulose Iα and Iβ' were 100% Lorentzian, while peaks for non-crystalline cellulose were 50% Lorentzian/50% Gaussian.

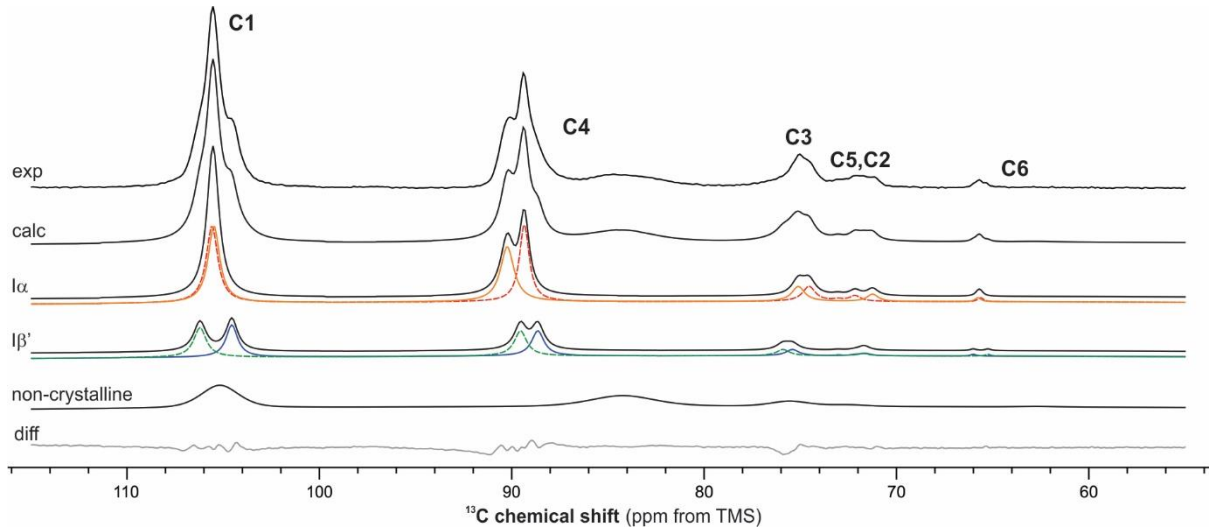

Fig. S3 Experimental 1D ^{13}C CP MAS NMR spectrum of bacterial cellulose ^{13}C-enriched at C1 and C4, along with the best-fit calculated model spectrum which is composed of contributions from cellulose Iα, cellulose Iβ', and non-crystalline cellulose. See Table S3 below for fitting parameters

Table S3 Model spectrum parameters for the calculated ^{13}C CP MAS NMR spectrum of bacterial cellulose ^{13}C-enriched at C1 and C4 displayed above in Fig. S3

	Chemical shift (ppm)	Peak width (ppm)	Peak area (%)		Chemical shift (ppm)	Peak width (ppm)	Peak area (%)
Glucose unit 1 of **Cellulose Iα**				**Glucose unit 2** of **Cellulose Iα**			
C1(α1)	105.58	0.72	12.85	C1(α2)	105.48	0.72	12.85
C2(α1)	72.17	0.67	0.85	C2(α2)	71.23	0.67	0.85
C3(α1)	74.56	0.80	2.75	C3(α2)	75.12	0.80	2.75
C4(α1)	89.35	0.60	10.74	C4(α2)	90.24	0.85	10.74
C5(α1)	73.05	0.67	0.27	C5(α2)	71.33	0.67	0.27
C6(α1)	65.64	0.34	0.32	C6(α2)	65.77	0.34	0.32
Glucose unit 1 of **Cellulose Iβ'**				**Glucose unit 2** of **Cellulose Iβ'**			
C1(β'1)	104.55	0.72	5.37	C1(β'2)	106.21	0.79	5.37
C2(β'1)	71.65	0.67	0.36	C2(β'2)	71.75	0.67	0.36
C3(β'1)	75.42	0.80	1.15	C3(β'2)	75.91	0.80	1.15
C4(β'1)	88.65	0.78	4.49	C4(β'2)	89.55	0.78	4.49
C5(β'1)	72.17	0.67	0.11	C5(β'2)	73.05	0.67	0.11
C6(β'1)	66.02	0.34	0.13	C6(β'2)	65.26	0.34	0.13
Non-crystalline cellulose							
C1(nc)	105.18	2.32	9.81				
C2(nc)	72.53	2.32	0.65				
C3(nc)	75.62	2.32	2.10				
C4(nc)	84.24	4.01	8.20				
C5(nc)	74.70	2.32	0.21				
C6(nc)	62.70	2.32	0.24				

* The peaks for cellulose Iα and Iβ' were 100% Lorentzian, while peaks for non-crystalline cellulose were 50% Lorentzian/50% Gaussian.

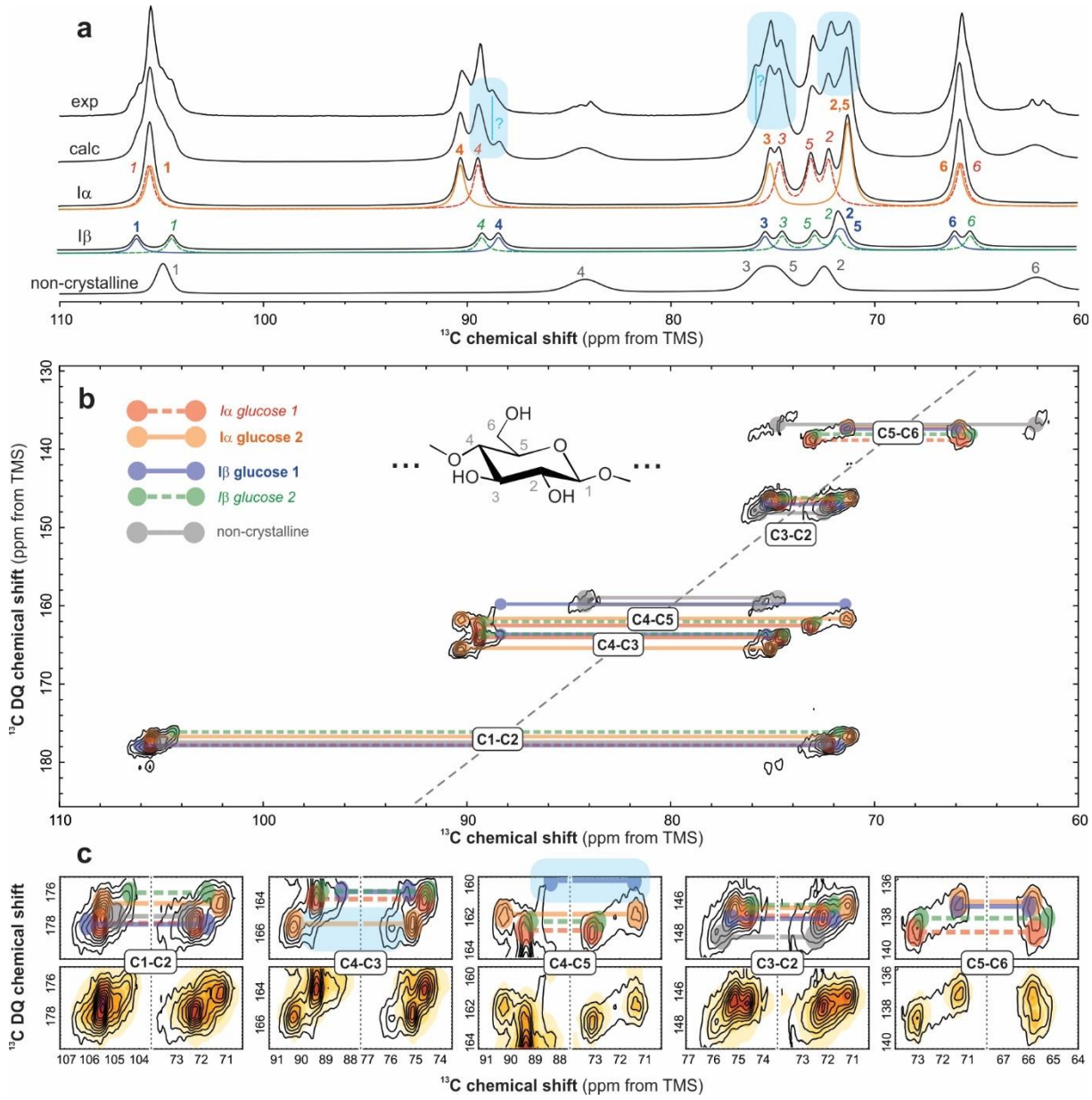

Fig. S4 Same as Fig. 3 in the main paper, except with ^{13}C chemical shifts and peak assignments for the cellulose Iβ sub-spectrum derived from tunicate cellulose (see Table 1 for chemical shifts). Regions of significant deviation from the experimental spectra are highlighted in light blue

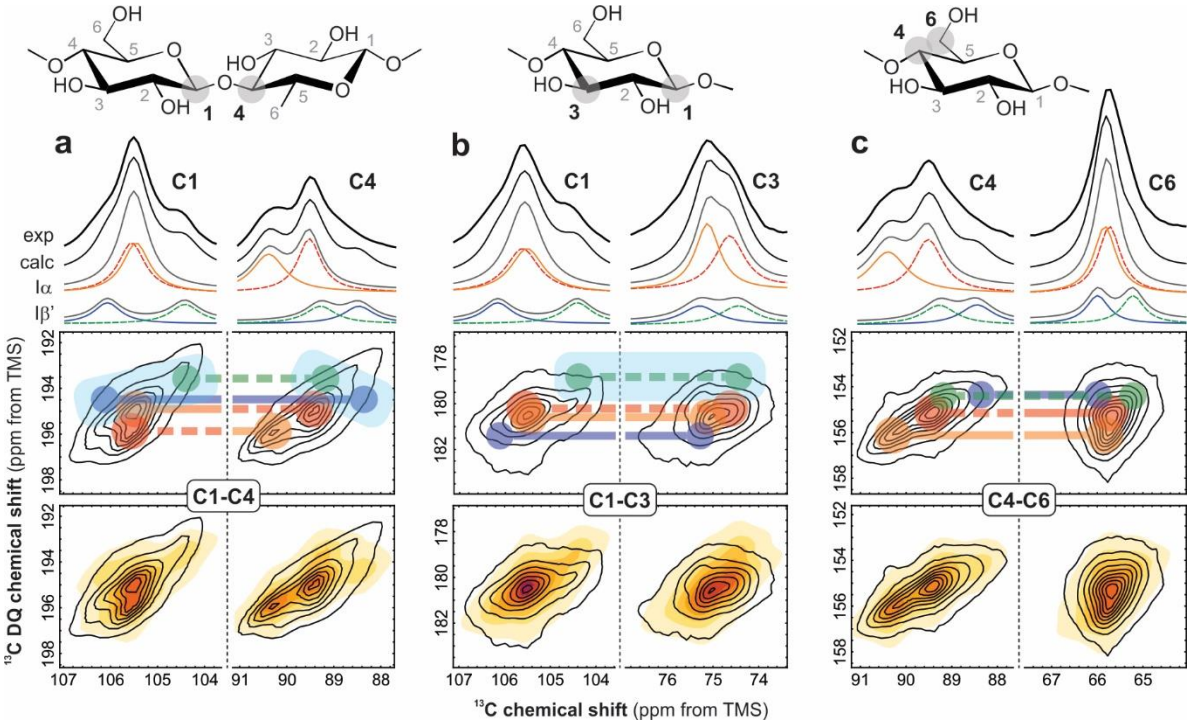

Fig. S5 Same as Fig. 4 in the main paper, except with ^{13}C chemical shifts and peak assignments for the cellulose Iβ sub-spectrum derived from tunicate cellulose (see Table 1 for chemical shifts). Regions of significant deviation from the experimental spectra are highlighted in light blue