Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Polymorphism of chitosan-based networks stabilized by phytate investigated by molecular dynamics simulations

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Table S1. The atom charges in the united atom representation for the chitosan and phytate

Chitosan			Phytate		
Atom type	Atom Name	Charge(*e* unit)	Atom type	Atom Name	Charge(*e* unit)
CH1R	C1	0.464	C	C	-0.015
	C2	0.197		C2	0.142
				C3	0.016
	C3 C4 C5	0.232		C4	-0.040
CH2	C6	0.232	Cpos	C1	0.198
				C5	0.258
OA	O1 O3 O4 O6	-0.642	OAlc	O18	-0.406
				O19	-0.457
				O20	-0.437
				O21	-0.443
				O22	-0.421
				O23	-0.464
OR	O5	-0.464	OM	O	-0.766
				O1	-0.749
				O2	-0.762
				O3	-0.756
				O4	-0.771
				O5	-0.753
				O6	-0.759
				O8	-0.718
				O11	-0.765
				O12	-0.721
				O14	-0.797
				O16	-0.754
NT (CHT0, CHTN	N2	-0.845	OEOp	O7	-0.705
				O9	-0.701
				O10	-0.697
				O13	-0.701
				O15	-0.709
				O17	-0.690

NL (CHTP)	N2	-0.448	P	P	1.013
				P1	1.018
				P2	0.975
				P3	1.038
				P4	1.022
				P5	1.007
H	HO1 HO3	0.410	HC	H	0.097
	HO4 HO6			H1	0.097
	H21 H22 H23	0.324		H2	0.125
		0.407 – CHTP		H3	0.114
				H4	0.091
				H5	0.078
			HS14	H7	0.435
				H9	0.459
				H10	0.436
				H13	0.460
				H15	0.444
				H17	0.434

Table S2. Lennard-Jones interaction parameters for the atom types

Atom type	C_6 (kJ mol^{-1} nm^6)	C_{12} (kJ mol^{-1} nm^{12})
CH1R	0.00606841	9.70225e-05
CH2	0.0074684164	3.3965584e-05
CPos	0.002025	1e-06
OA	0.0022619536	1.505529e-06
OR	0.0022619536	1.21e-06
OM	0.0022619536	7.4149321e-07
OEOp	0.00308914	4.77422e-06
OAlc	0.00177494	1.21e-06
NT	0.0024364096	5.0625e-06
NL	0.0024364096	2.319529e-06
P	0.01473796	2.2193521e-05
H	0	0
HC	8.464e-05	1.5129e-08
HS14	0	0

* other parameters for special intramolecular Lennard-Jones interactions can be found in Table 10 of ref. (Naumov & Ignatov, 2017)

Table S3. Parameters for the bond interactions.

Bond type	b_0 (nm)	K_b (10^6 kJmol^{-1}nm^{-4})
Chitosan		
CH1R-OA, CH1R-OR, CH2-OA	0.1435	6.1000e+06
CH1R-CH1R, CH1R-CH2	0.1520	5.4300e+06
OA-H	0.1000	1.5700e+07
CH1R-NT,NL	0.1470	8.7100e+06
NT,NL-H	0.1000	1.8700e+07
NT,NL-C	0.1340	1.0500e+07
Phytic acid		
C-C	0.1540	4.2166e+06
C-Cpos	0.1560	3.0819e+06
Cpos-OAlc	0.1420	3.2236e+06
C-OAlc	0.1410	6.5389e+06
	0.1430	8.1800e+06
C-HC	0.1090	1.2300e+07
OEOp-HS14	0.1010	1.5700e+07
	0.1000	2.1076e+07
OEOp-P	0.1630	4.7200e+06
OM-P	0.1530	7.1500e+06
	0.1500	8.3700e+06
	0.1510	3.7279e+06
OAlc-P	0.1660	2.9032e+06
	0.1670	3.0478e+06

Table S4. Number of H-bonds between the CT residues and PA averaged over the last 50 ns simulation time.

System	Residue type	
	CHTP (charged)	CHT0, CHTN, CHT (uncharged)
CT-083-10	98±4.9	8.7±2.2
CT-050-10	75±4.6	36.6±3.1
CT-033-10	56±4.1	48.2±4.4

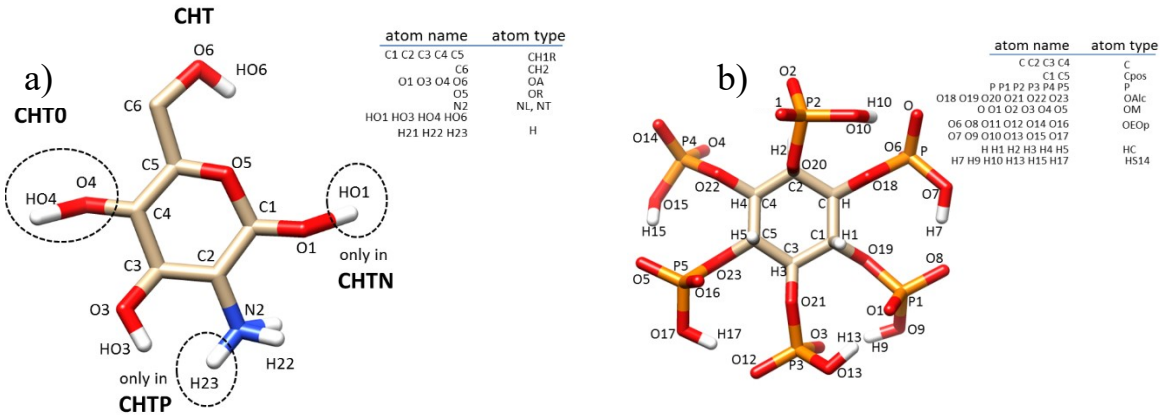

Figure S1. a) Types of monomers for the chitosan chain description and names and types of atoms according to the implemented force field; b) atom names and types for the atomistic representation of the phytate ion(cis-1,2,3,5-trans-4,6-cyclohexanehexol hexakisphosphate); the myo-isomer with five equatorial phosphate substituents at C, C1, C3, C5 and C4 and one axial phosphate substituent at C2 is shown in b).

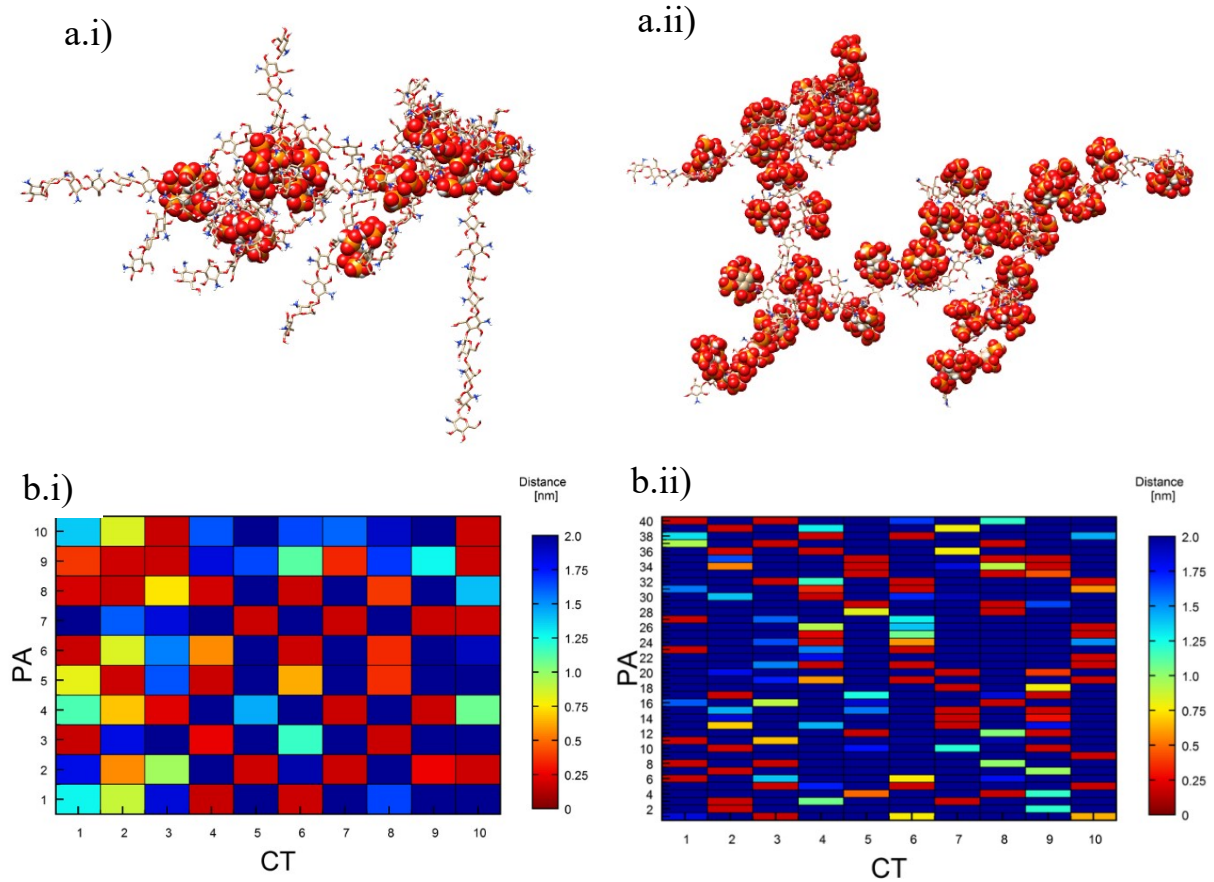

Figure S2. a) Snapshot of the final configuration and b) and minimum distance between CT and PA averaged over the last 50 ns simulation time interval for i) CT-083-10 and ii) CT-083-40; the water and counterions were omitted in a) for clarity sake.

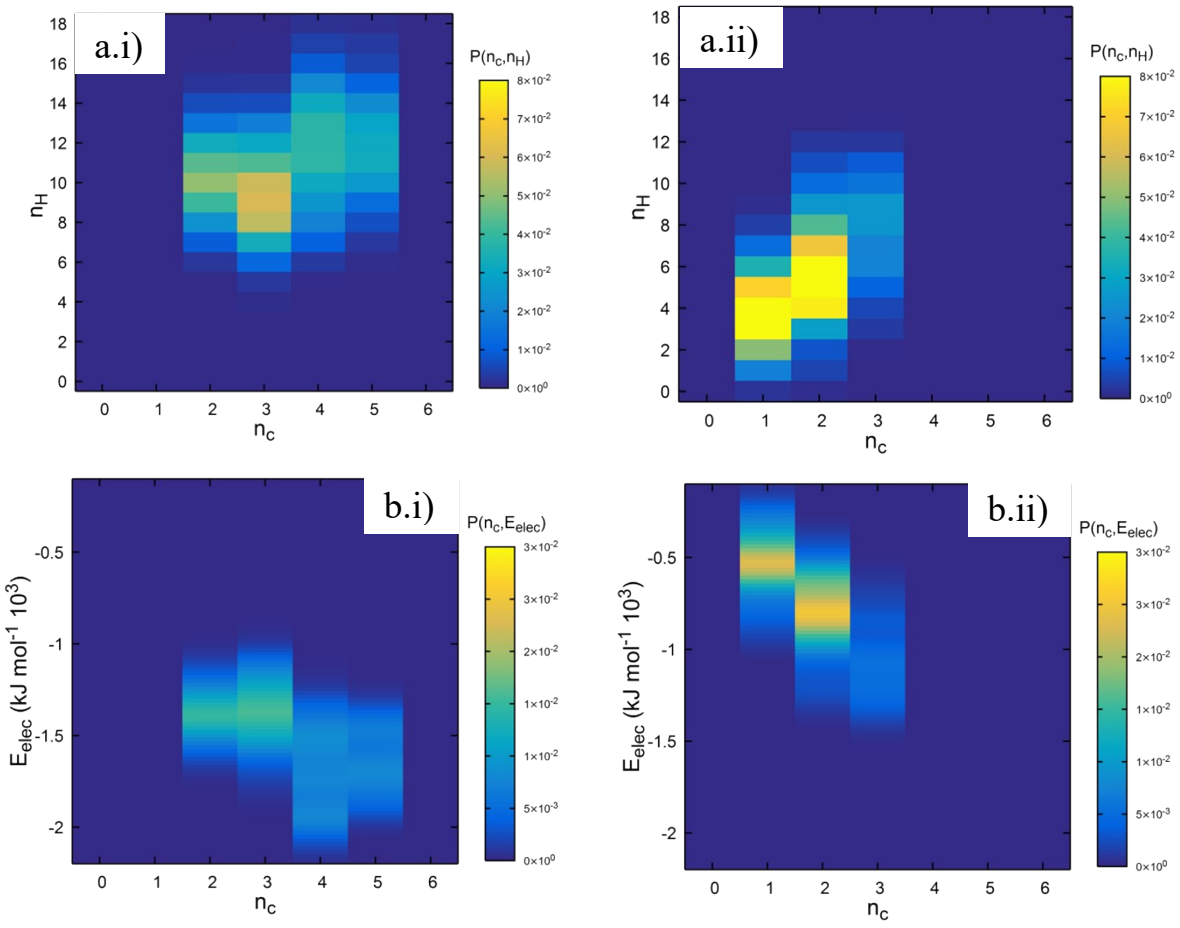

Figure S3. Probability distribution of the number of crosslinked chitosan chains by a PA n_c and a) H bond number n_H and b) electrostatic energy E_{elec} between anion and chitosan for i) CT-083-10, ii) CT-083-40

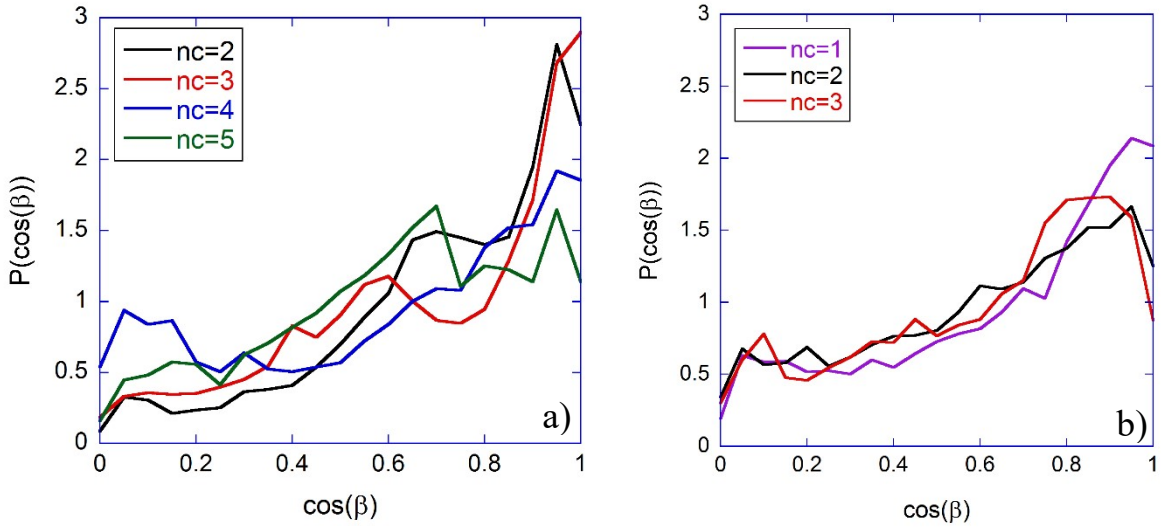

Figure S4. Probability distribution of the angle made by the inositol with the closest glucopyranose rings at the indicated number of crosslinked chains for a) CT-083-10, b) CT-083-40.

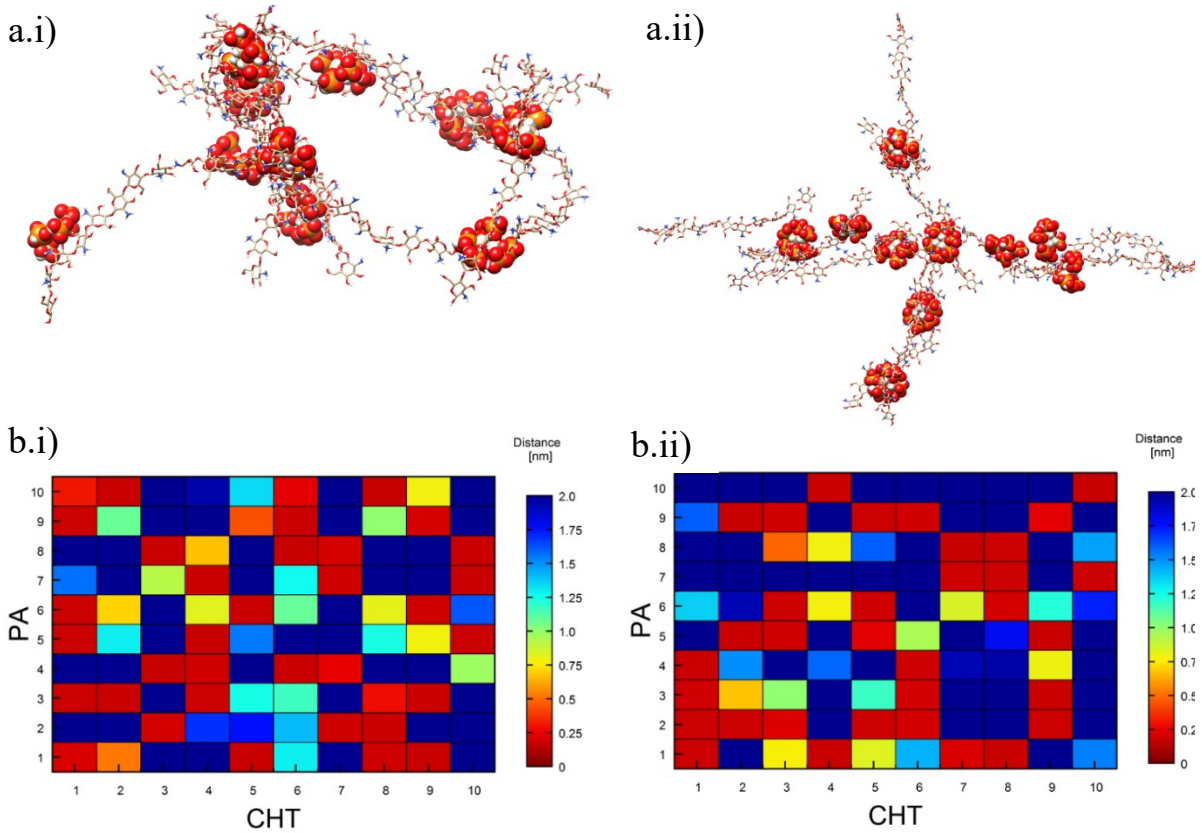

Figure S5. a) Snapshot of the final configuration and b) and minimum distance between CT and PA averaged over the last 50 ns simulation time interval for i) CT-050-10 and ii) CT-033-10.

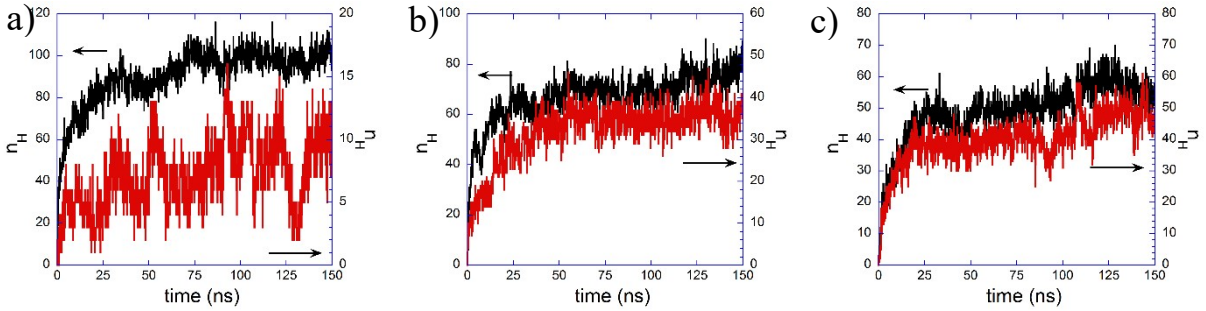

Figure S6. The time evolution of H bond number made by PA with charged (black curves) and uncharged (red curves) CT monomers for i) CT-83-10, ii) CT-50-10 and iii) CT-33-10.

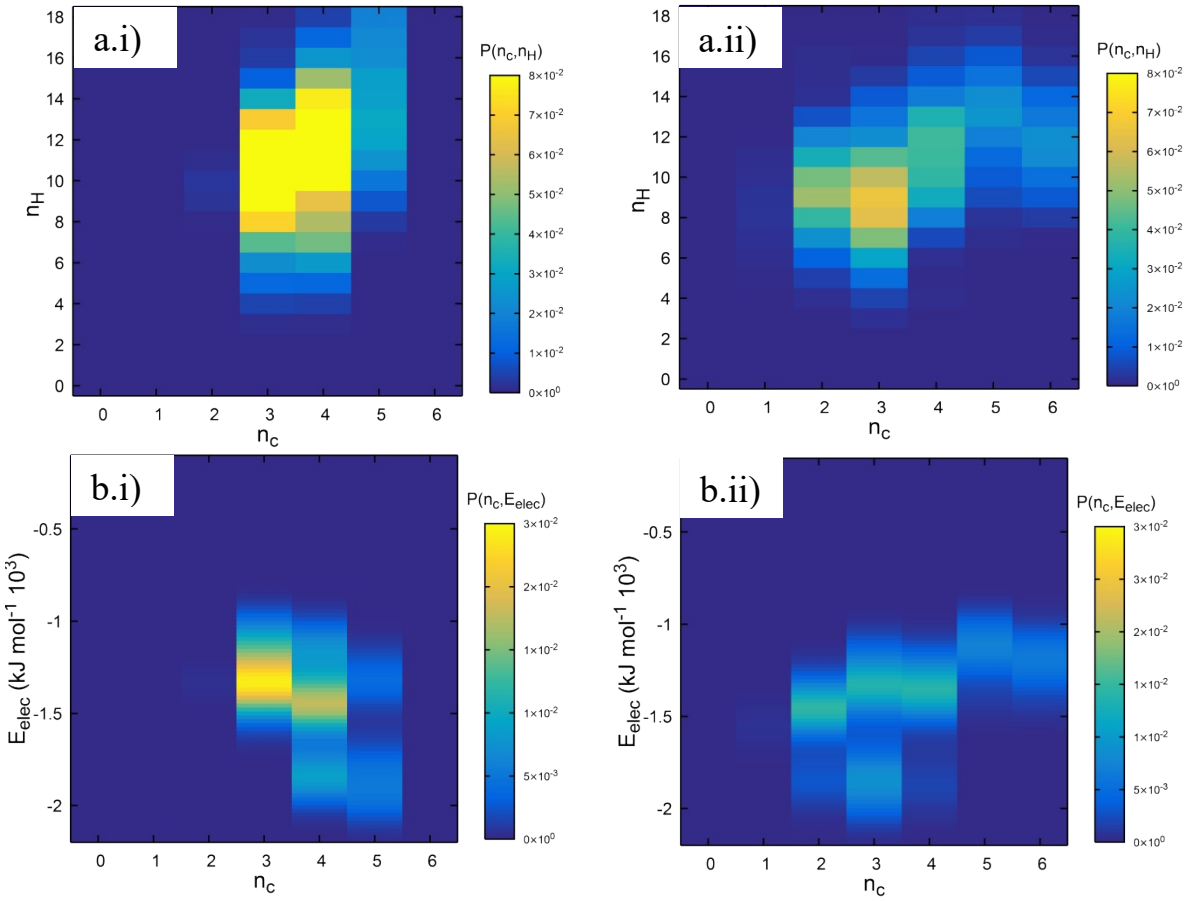

Figure S7. Probability distribution of the number of crosslinked chitosan chains by a PA n_c and a) H bond number n_H and b) electrostatic energy E_{elec} between the anion and chitosan chains for i) CT-050-10 and ii) CT-033-10.

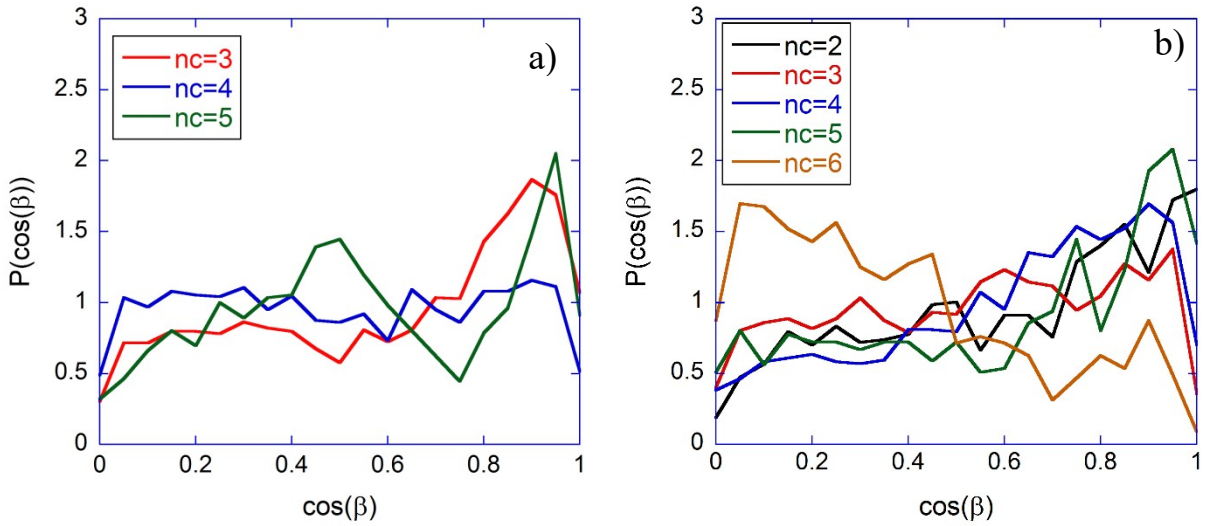

Figure S8. Probability distribution of the angle made by the inositol with the closest glucopyranose rings at the indicated number of crosslinked chains for a) CT-050-10, b) CT-033-10.

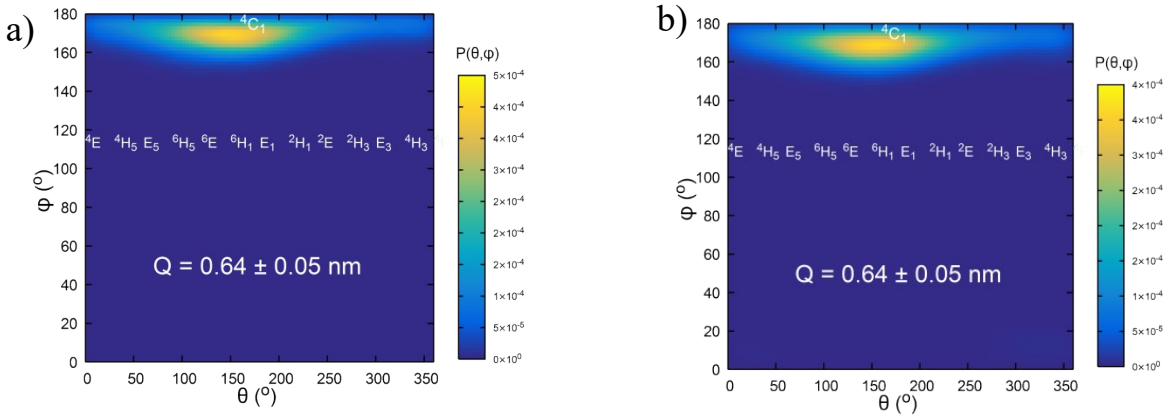

Figure S9. Probability distribution of puckering phase angles, θ and φ for pyranose in a) CT-water system and b) CT-083-5. The puckering amplitude Q and location of the closest characteristic ring conformers (^{4}E … ^{4}H$_3$) are also given.

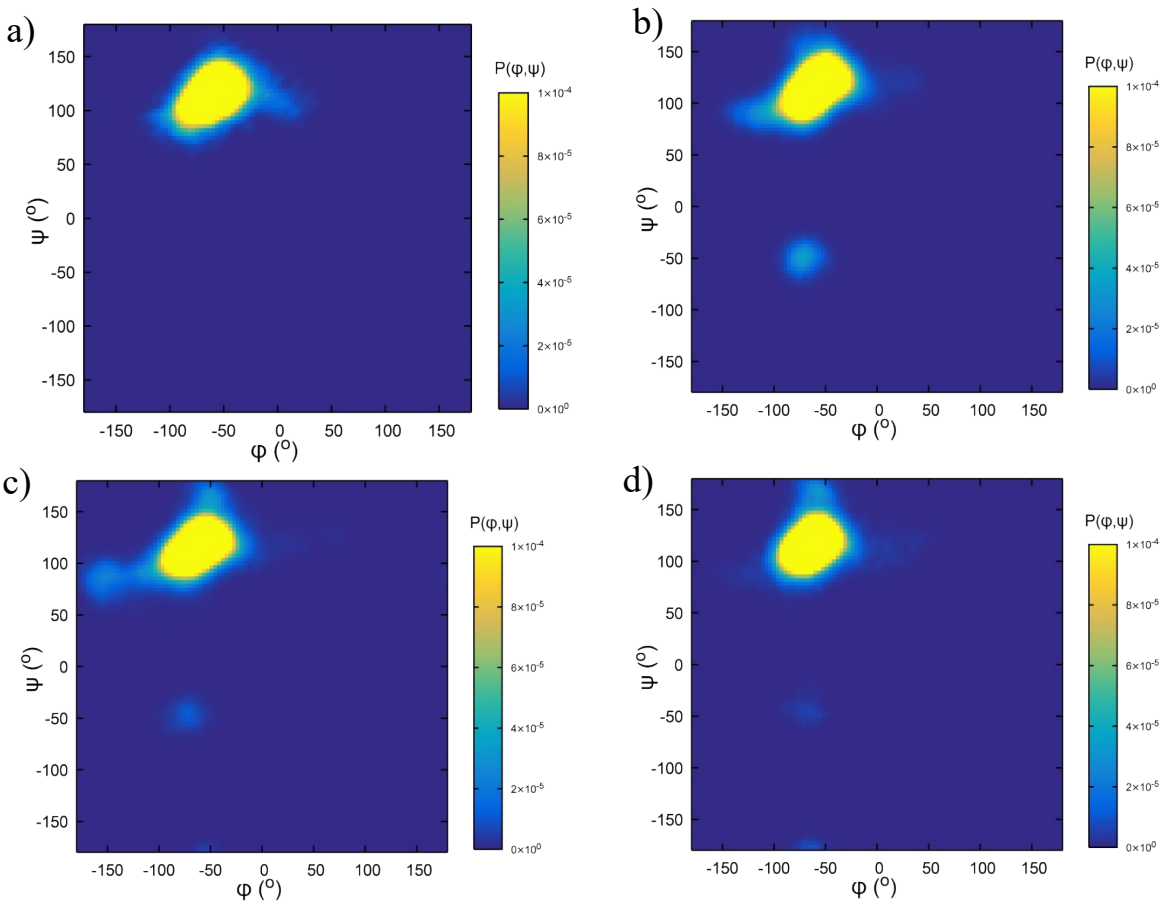

Figure S10. Probability distribution of the torsional angles of the chitosan chains φ and ψ for a) CT-083-10, b) CT-083-40, c) CT-050-10, d) CT-033-10.

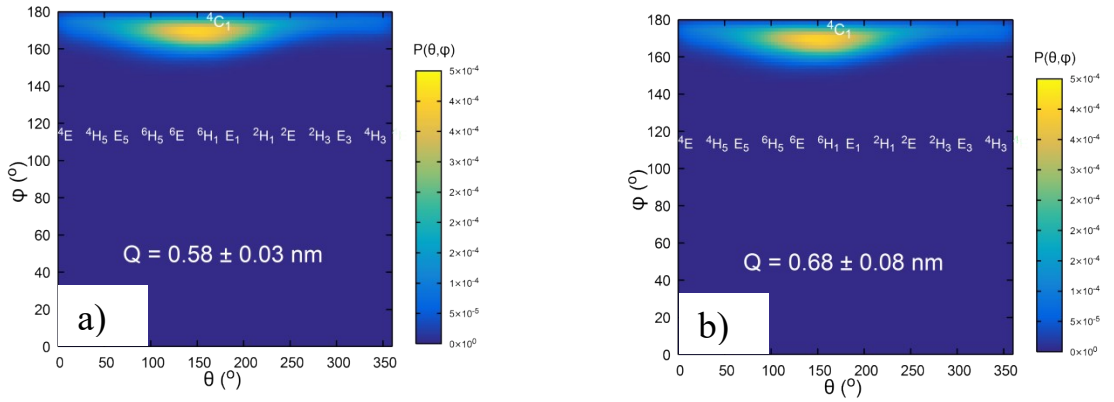

Figure S11. Probability distribution of puckering phase angles, θ and φ of the inositol ring in a) phytate-water system and b) CT-083-5. The puckering amplitude Q and location of the closest characteristic ring conformers (^{4}E … ^{4}H$_3$) are also given.

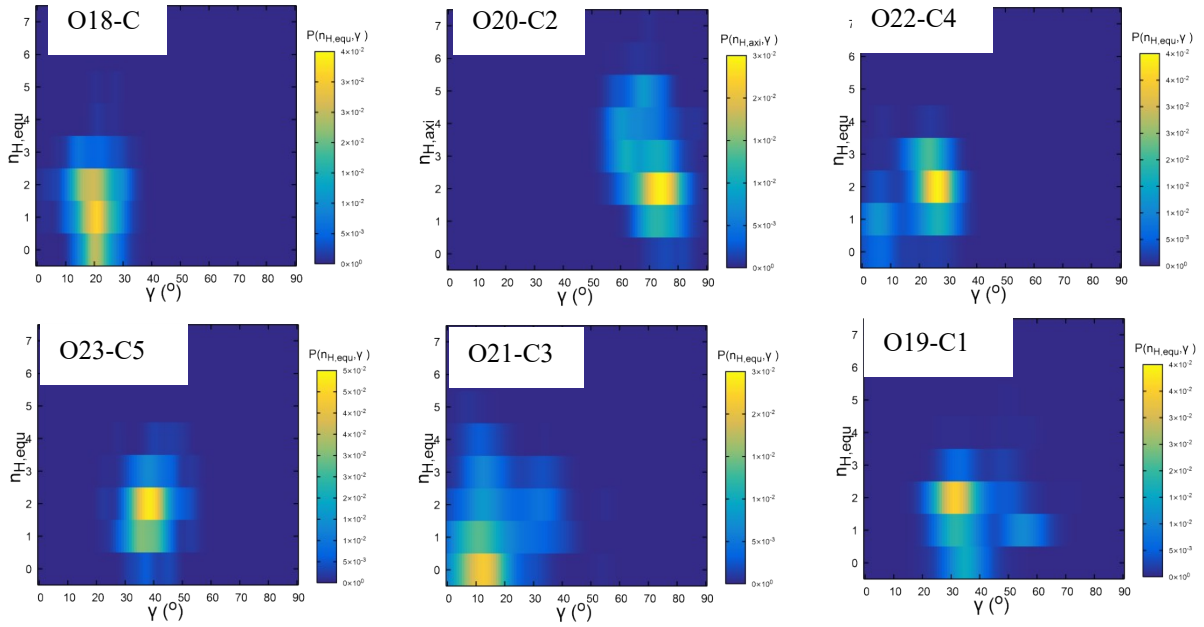

Figure S12. Pair probability distribution $P(\gamma,n_H)$ of the angle γ made by C-O bonds with main plane of inositol and H bond number n_H of the phosphates substituted at the indicated inositol positions for CT-083-5.

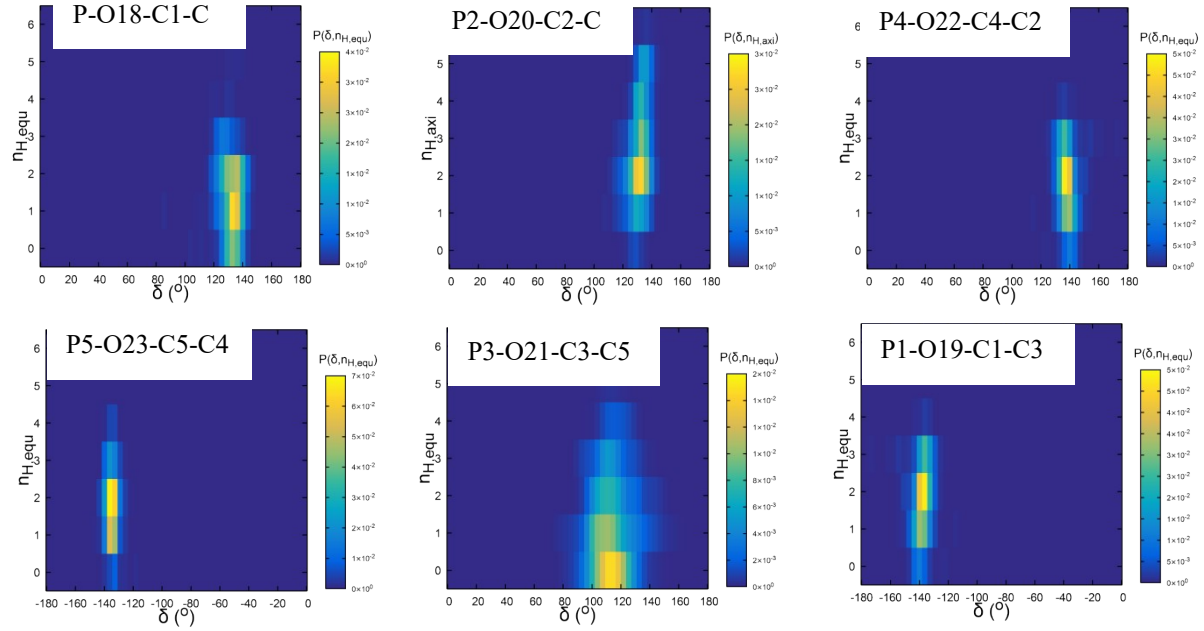

Figure S13. Pair probability distribution $P(\delta,n_H)$ of dihedral angle along the six phosphoester bonds δ and the H bond number n_H of the phosphates substituted at the indicated inositol positions in CT-083-5.