Insights on the Cellulose Pretreatment at room Temperature by Choline-Chloride-based Deep Eutectic Solvents: An Atomistic Study.

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Table S1 DESs, cellulose-DES, and isolated molecule systems evaluated in this work with their respective HBA:HBD molar ratio[a]

System name	HBD	HBA:HBD Molar ratio	Number of molecules in the system	Equilibrated *NPT* cubic length size, [$\dot{A}$]
ChCl/ethylene glycol	ethylene glycol	1:2	1455:2910	83.16
ChCl/oxalic acid	oxalic acid	1:1	1885:1885	83.47
ChCl/urea	urea	1:2	1587:3174	84.16
ChCl/levulinic acid	levulinic acid	1:2	1052:2104	83.05
Single glucan			12 D-glucose units (DP = 12[b])	200
cellulose crystallite			39 glucans, DP = 12[b]	-
cellulose-ChCl/ethylene glycol	ethylene glycol	1:2	39:1455:2910	86.9
cellulose-ChCl/oxalic acid	oxalic acid	1:1	39:1885:1885	87.29
cellulose-ChCl/urea	urea	1:2	39:1587:3174	87.8
cellulose-ChCl/levulinic acid	levulinic acid	1:2	39:1052:2104	86.91
ChCl/ethylene glycol	ethylene glycol	1:2	1:2	100
ChCl/oxalic acid	oxalic acid	1:1	1:1	100
ChCl/urea	urea	1:2	1:2	100
ChCl/levulinic acid	levulinic acid	1:2	1:2	100

[a] The HBA in all DESs and cellulose-DES systems was choline-chloride (ChCl).
[b] DP: degree of polymerization.

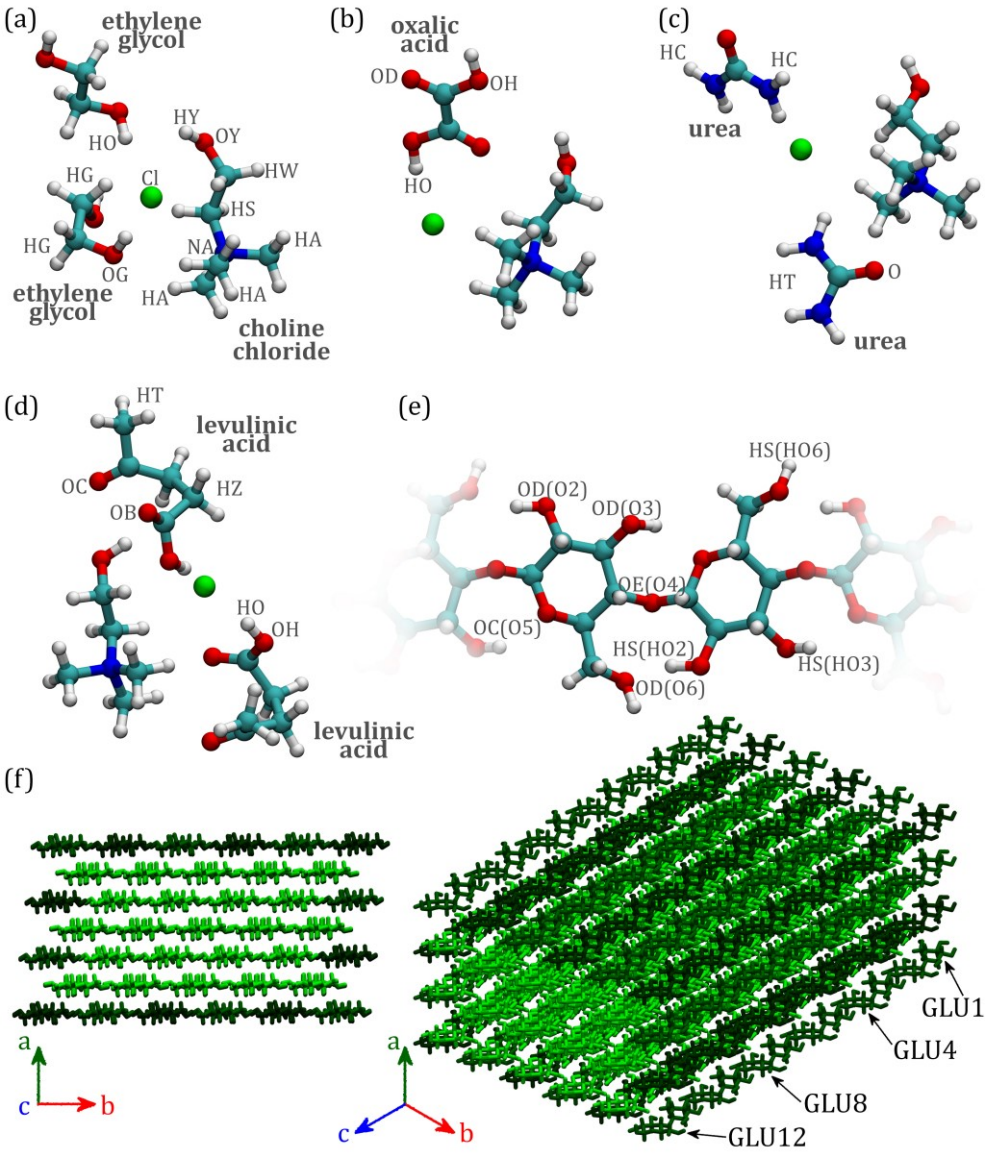


Fig. S1 Atomic labels and molecular structures for the deep eutectic solvents and cellulose crystallite modeled in this work. **a** Choline-chloride ethylene glycol (ChCl/ethylene glycol) with 1:2 HBA:HBD molar ratio. **b** Choline-chloride oxalic acid (ChCl/oxalic acid, 1:1). **c** Choline-chloride urea (ChCl/urea, 1:2). **d** Choline-chloride levulinic acid (ChCl/levulinic acid, 1:2). **e** Glucan atom labeling, including the commonly used atom numbering (in parenthesis); the OD atom refers to the oxygen atom in the hydroxyl group, the OC atom includes the oxygen atom within the six-member ring, and the HS atom denotes the hydrogen atom attached to OD atom. **f** Cellulose crystallite composed by 39 glucan of 12 glucose units (GLU residues) each as indicated, arranged in seven layers; left**:** projection onto the a-b base plane, right: isometric projection. Glucan in these pictures have been green-scale colored for clarity. Color/atom code: blue/nitrogen, green/chlorine, grey/carbon, red/oxygen, and white/hydrogen. All images have been created with the visual molecular dynamics (VMD) software (Humphrey et al. 1996)

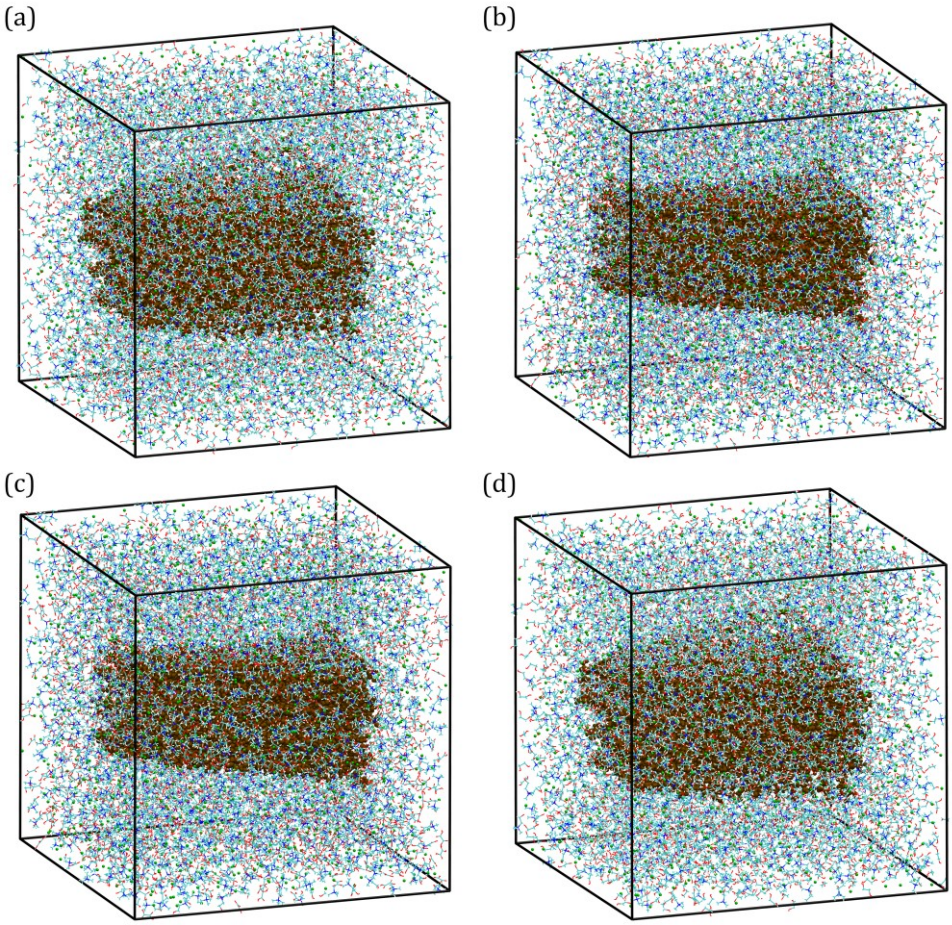


Fig. S2 Final configuration of cellulose-DES systems. **a** Cellulose-ChCl/ethylene glycol, **b** Cellulose-ChCl/oxalic acid, **c** Cellulose-ChCl/urea, and **d** Cellulose-ChCl/levulinic acid. The equilibrated cubic box lengths are 86.9, 87.29, 87.8, and 86.91 $\dot{A}$, respectively

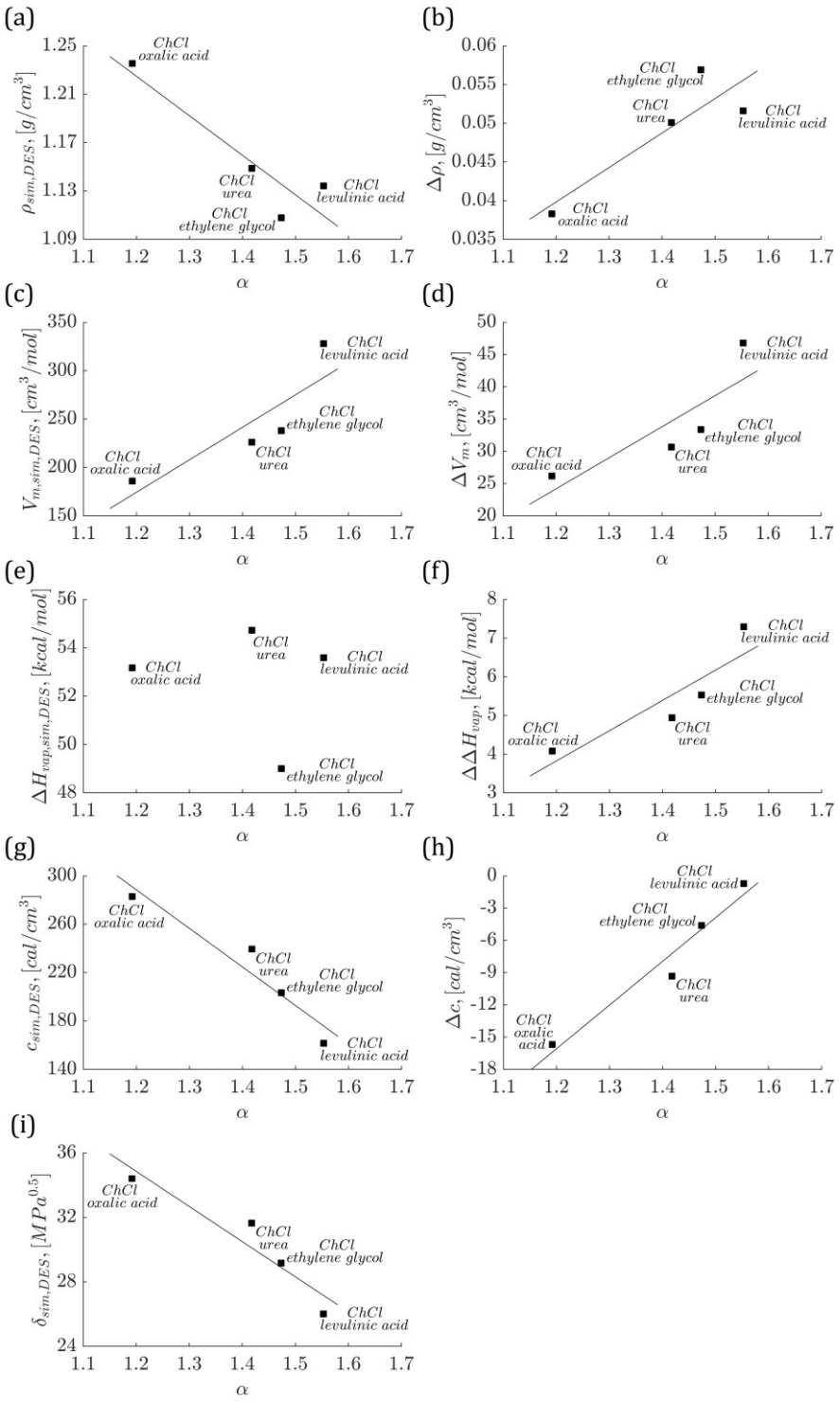


Fig. S3 Linear correlations observed between the Kamlet-Taft α parameter and: **a** Density ($\rho_{sim,solvent}$, $R^2 = 0.84$), **b** Density change ($\Delta\rho$, $R^2 = 0.78$), **c** Molar volume ($V_{m,sim}$, $R^2 = 0.75$), **d** Molar volume change (ΔV_m, $R^2 = 0.71$), **e** Enthalpy of vaporization ($\Delta H_{vap,sim}$, $R^2 = 0.03$), **f** Enthalpy of vaporization change ($\Delta\Delta H_{vap}$, $R^2 = 0.80$), **g** Cohesive energy density (c_{sim}, $R^2 = 0.91$), **h** Cohesive energy density change (Δc, $R^2 = 0.95$), and **i** Hildebrand parameter (δ, $R^2 = 0.89$)

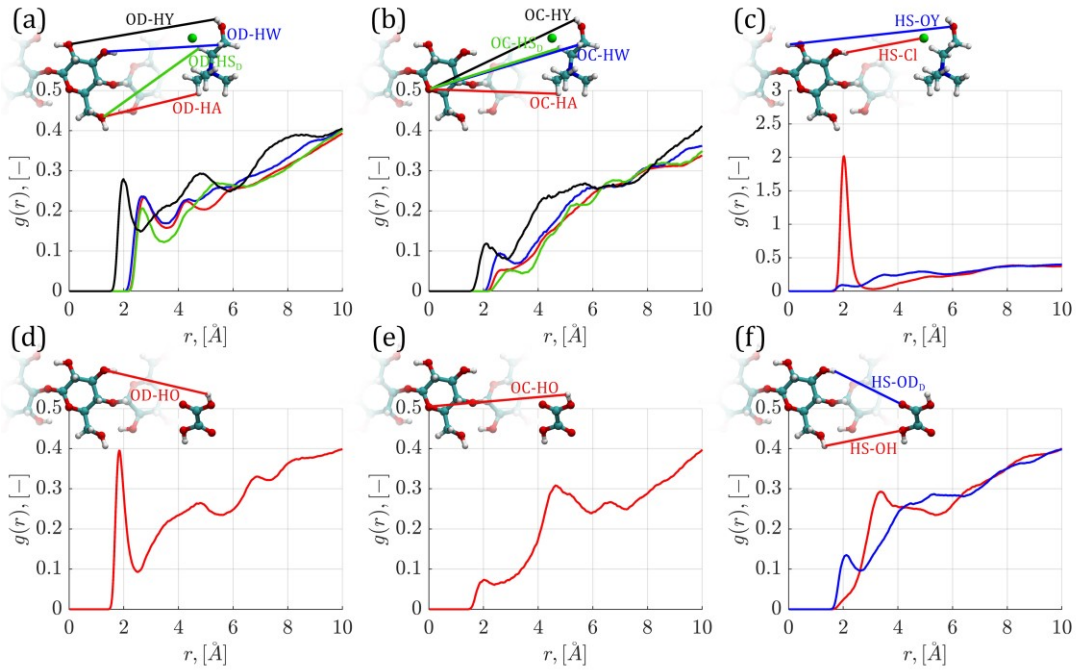


Fig. S4 RDFs for searching possible HBs between cellulose crystallite (OD, OC, and HS atoms) and ChCl/oxalic acid (HA, HW, HS_D, HY, HO, Cl, OY, OD_D, and OH atoms) in the cellulose-ChCl/oxalic acid system. The interactions involved: **a** OD oxygen atoms from glucose units and hydrogen atoms from choline cation. **b** OC oxygen atoms from glucose units and hydrogen atoms from choline cation. **c** HS hydrogen atoms from glucose units and OY oxygen atom from choline cation and chloride anion. **d** OD oxygen atoms from glucose units and hydrogen atoms from oxalic acid HBD. **e** OC oxygen atoms from glucose units and hydrogen atoms from oxalic acid HBD. **f** HS hydrogen atoms from glucose units and oxygen atoms from oxalic acid HBD. Atomic labels are also shown in Fig. S1

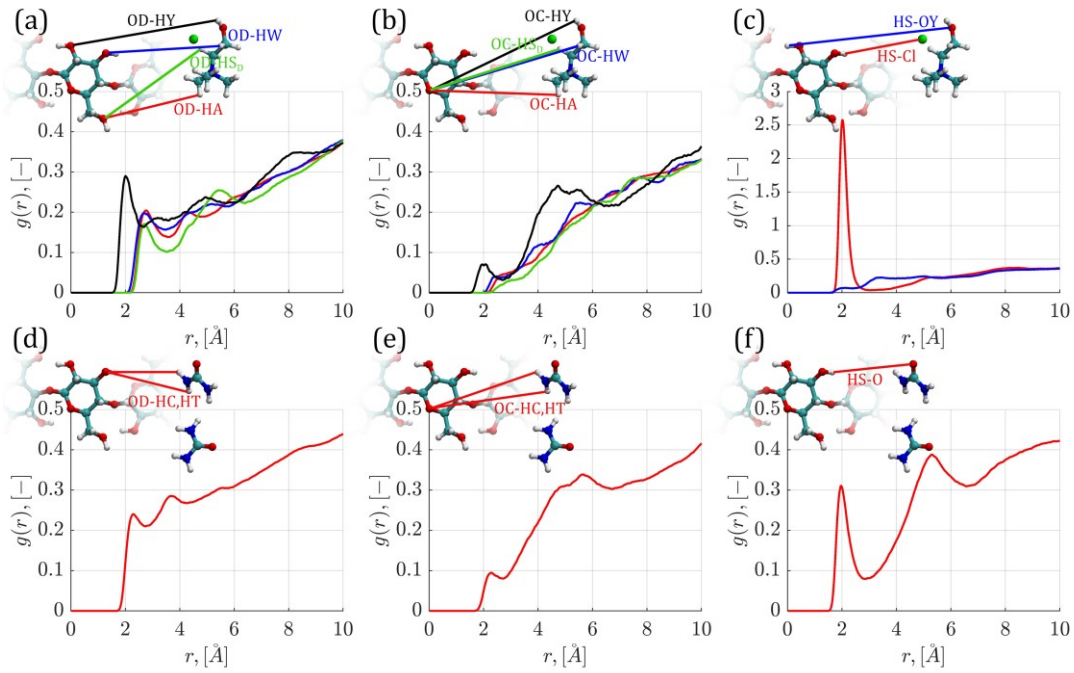


Fig. S5 RDFs for searching possible HBs between cellulose crystallite (OD, OC, and HS atoms) and ChCl/urea (HA, HW, HS_D, HY, HC, HT, Cl, OY, and O atoms) in the cellulose-ChCl/urea system. The interactions involved: **a** OD oxygen atoms from glucose units and hydrogen atoms from choline cation. **b** OC oxygen atoms from glucose units and hydrogen atoms from choline cation. **c** HS hydrogen atoms from glucose units and OY oxygen atom from choline cation and chloride anion. **d** OD oxygen atoms from glucose units and hydrogen atoms from urea HBD. **e** OC oxygen atoms from glucose units and hydrogen atoms from urea HBD. **f** HS hydrogen atoms from glucose units and oxygen atoms from urea HBD. Atomic labels are also shown in Fig. S1

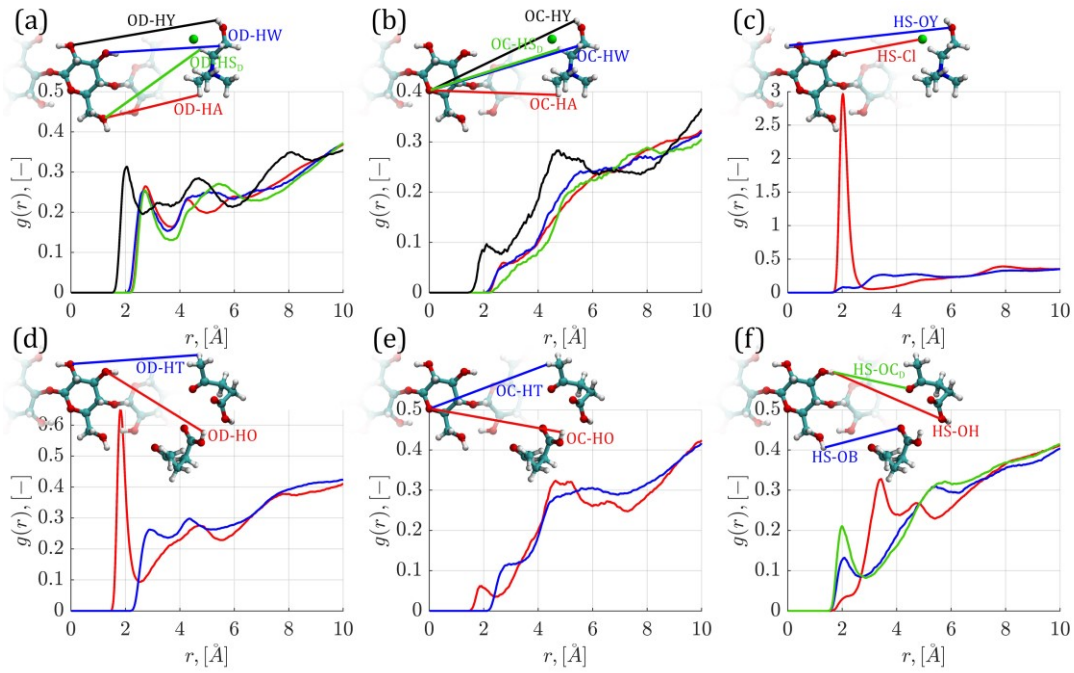


Fig. S6 RDFs for searching possible HBs between cellulose crystallite (OD, OC, and HS atoms) and ChCl/levulinic acid (HA, HW, HS_D, HY, HT, HO, Cl, OY, OB, OC_D, and OH atoms) in the cellulose-ChCl/levulinic acid system. The interactions involved: **a** OD oxygen atoms from glucose units and hydrogen atoms from choline cation. **b** OC oxygen atoms from glucose units and hydrogen atoms from choline cation. **c** HS hydrogen atoms from glucose units and OY oxygen atom from choline cation and chloride anion. **d** OD oxygen atoms from glucose units and hydrogen atoms from levulinic acid HBD. **e** OC oxygen atoms from glucose units and hydrogen atoms from levulinic acid HBD. **f** HS hydrogen atoms from glucose units and oxygen atoms from levulinic acid HBD. Atomic labels are also shown in Fig. S1

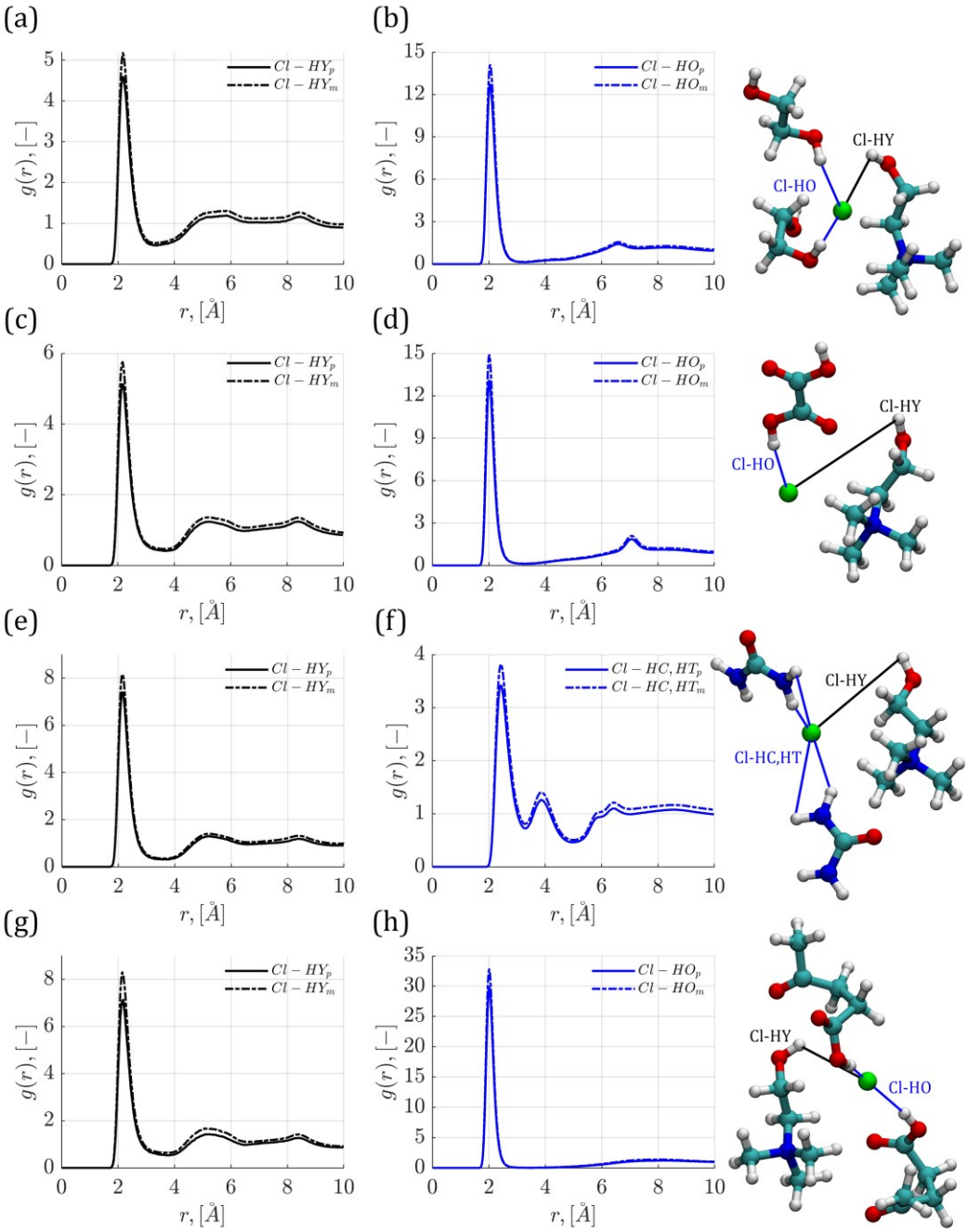


Fig. S7 RDFs for searching possible HBs within ChCl and between ChCl and HBD molecules in the pure DES (continues line) and cellulose-DES systems (dotted line) in **(a,b)** ChCl/ethylene glycol, **(c,d)** ChCl/oxalic acid, **(e,f)** ChCl/urea, and **(g,h)** ChCl/levulinic acid as solvent

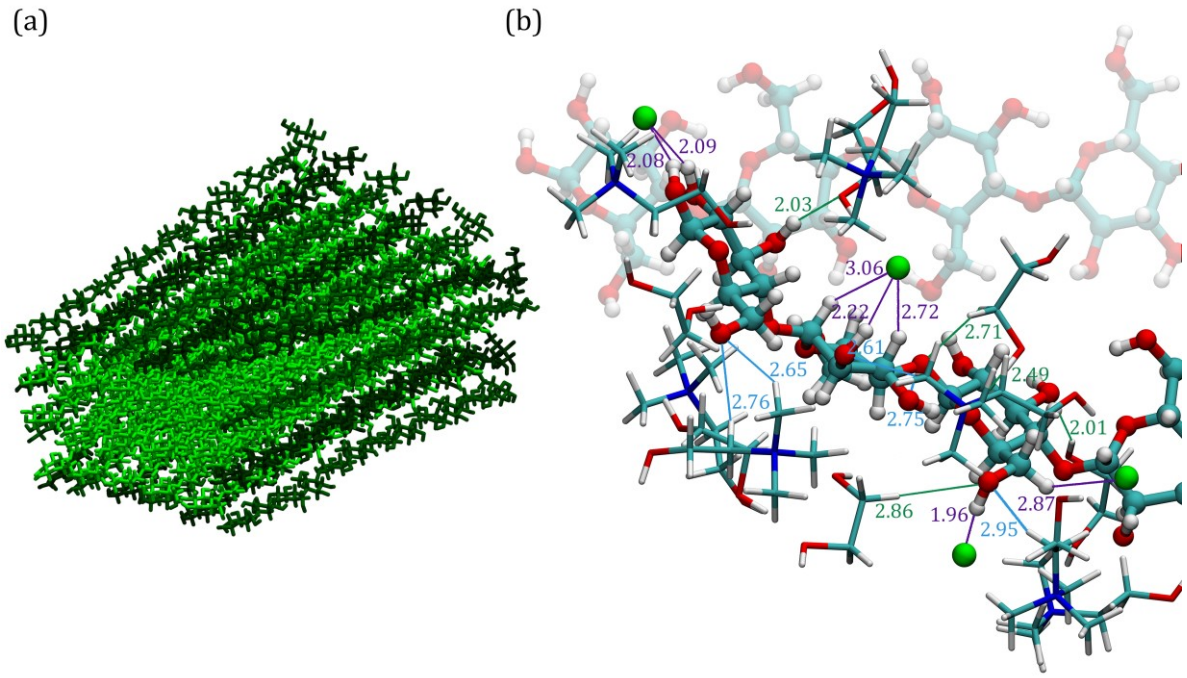


Fig. S8 Final molecular configuration of the cellulose crystallite in ChCl/ethylene glycol DES: **a** Main view and **b** Close view to the deformed chains and surrounded DES molecules. The atom-atom interactions lines in (b) are colored as follows: choline-cellulose/light blue, chloride-cellulose/dark blue, and HBD-cellulose/dark green. All distances in *Å*

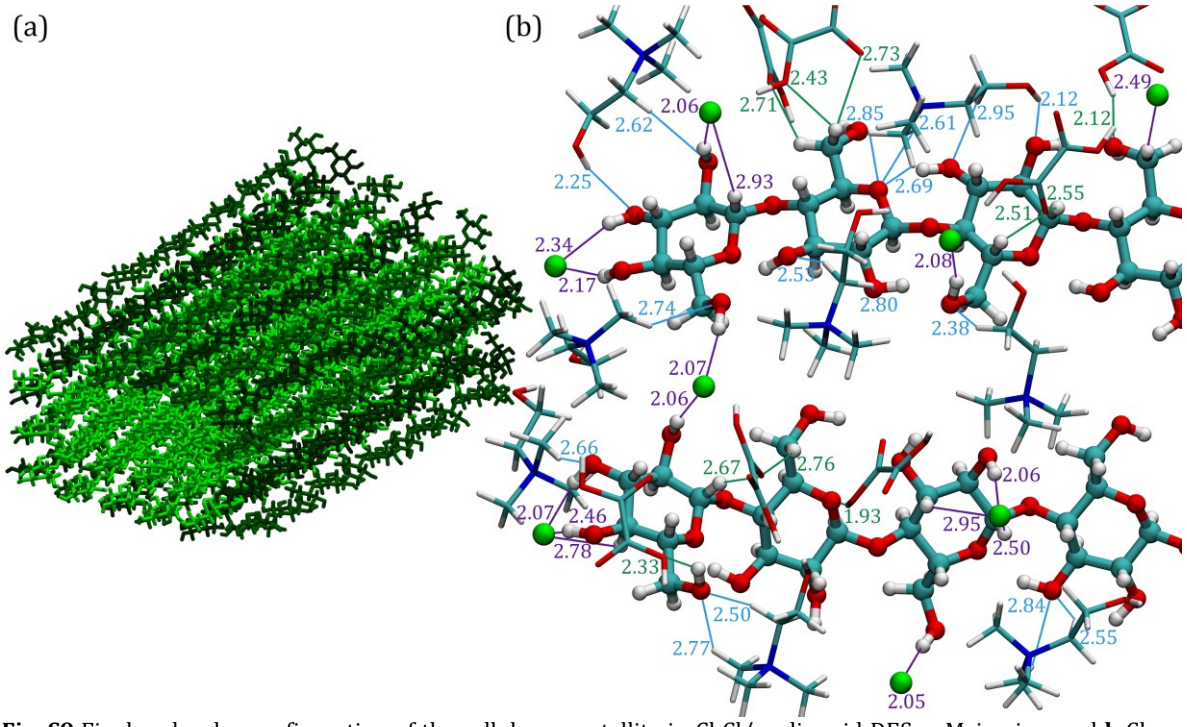


Fig. S9 Final molecular configuration of the cellulose crystallite in ChCl/oxalic acid DES: **a** Main view and **b** Close view to the deformed chains and surrounded DES molecules. The atom-atom interactions lines in (b) are colored as follows: choline-cellulose/light blue, chloride-cellulose/dark blue, and HBD-cellulose/dark green. All distances in *Å*

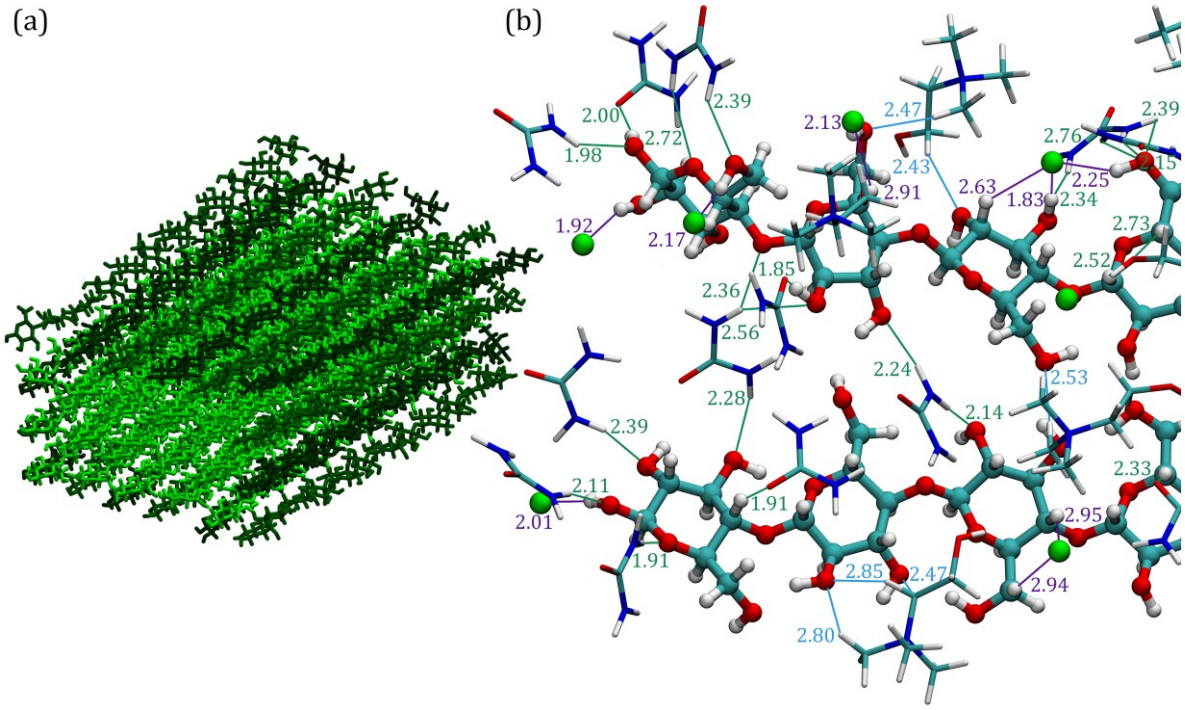


Fig. S10 Final molecular configuration of the cellulose crystallite in ChCl/urea DES: **a** Main view and **b** Close view to the deformed chains and surrounded DES molecules. The atom-atom interactions lines in (b) are colored as follows: choline-cellulose/light blue, chloride-cellulose/dark blue, and HBD-cellulose/dark green. All distances in *Å*

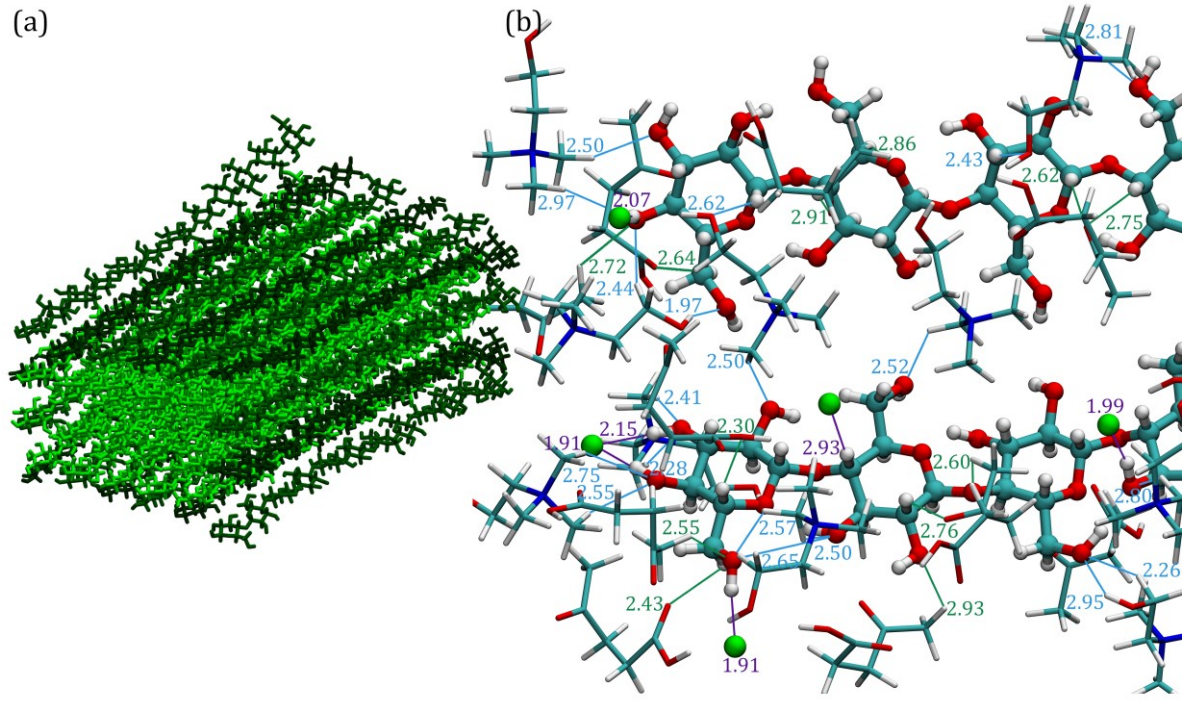


Fig. S11. Final molecular configuration of the cellulose crystallite in ChCl/levulinic acid DES: **a** Main view and **b** Close view to the deformed chains and surrounded DES molecules. The atom-atom interactions lines in (b) are colored as follows: choline-cellulose/light blue, chloride-cellulose/dark blue, and HBD-cellulose/dark green. All distances in *Å*

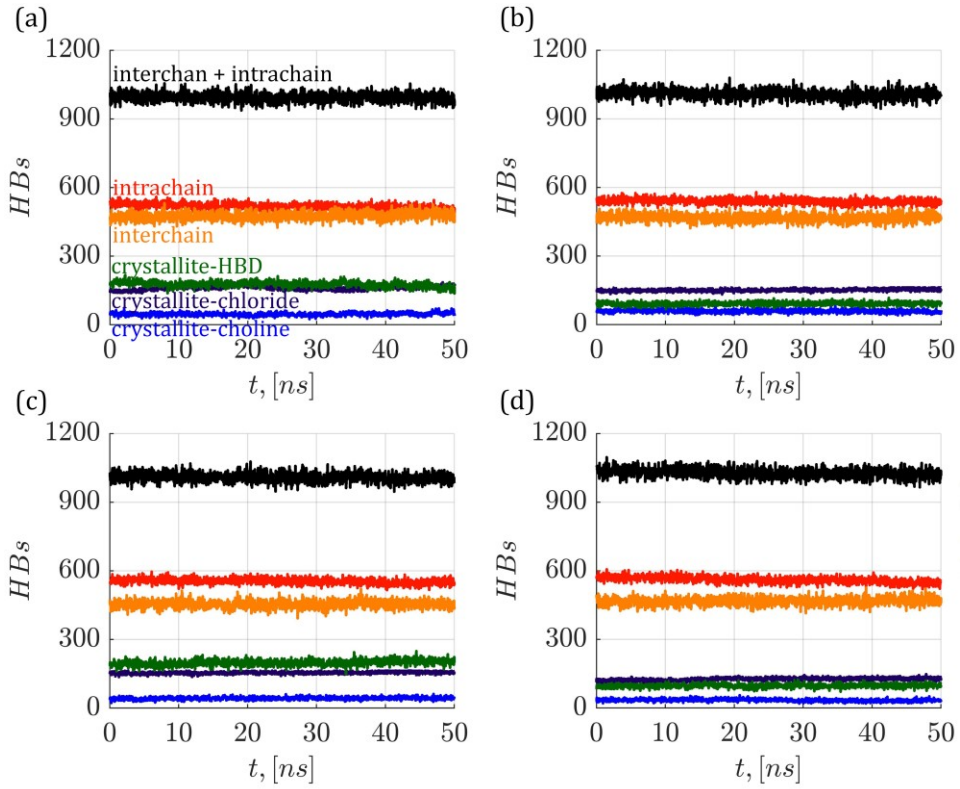


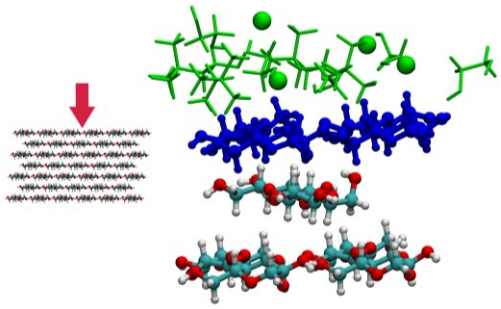
Fig. S12. Calculated HBs as function of time for: total (intrachain and interchain) HBs (black line), intrachain HBs (red line), interchain HBs (orange line), cellulose crystallite and choline cation HBs (blue line), cellulose crystallite and chloride anion HBs (dark-blue line), and cellulose crystallite and HBD (green line) in: **a** cellulose-ChCl/ethylene glycol, **b** cellulose-ChCl/oxalic acid, **c** cellulose-ChCl/urea, and **d** cellulose-ChCl/levulinic acid systems. HBs have been calculated with the Hydrogen Bonds plugin available in the VMD software (Humphrey et al. 1996)

Hydrogen bonds between cellulose unit cell and DES molecules. The cellulose unit cell, composed by five cellobiose (two glucose molecules linked by the β(1→4') glycosidic bond) molecules was extracted from the center top and from the (less disrupted) edge of the cellulose crystallite along with the DES molecules within 8 $\dot{A}$ from the unit cell. The missing $C-OH$ bonds in the glucose units were completed by using GaussView6 (Dennington et al. 2016) package. The molecular configuration of the system was minimized in the TeraChem (Ufimtsev and Martínez 2008) software at the PBE0 (Perdew et al. 1996, 1997; Adamo and Barone 1999)/6-311g** level of theory with empirical D3 dispersion corrections, (Grimme et al. 2010) maintaining the heavy atoms fixed, in order to directionally optimized all the HBs. After minimization, a single point energy calculation was evaluated at the same level of theory in TeraChem; the generated *molden* output file was then used to generate the electronic wave function through MOLDEN2AIM (Zou 2021) software. The non-covalent interactions were obtained through the analysis of the bond critical points of the electronic density ($\rho(\mathbf{r})$) in GPUAM (Hernández-Esparza et al. 2014, 2019; Cruz et al. 2019) package by using a mesh grid of 12 p/a.u. Finally, the attractive non-covalent interactions were identified by both the electronic density values and the sign of the laplacian of the $\rho(\mathbf{r})$ (Johnson et al. 2010; Contreras-García et al. 2011). Results from this analysis are shown in

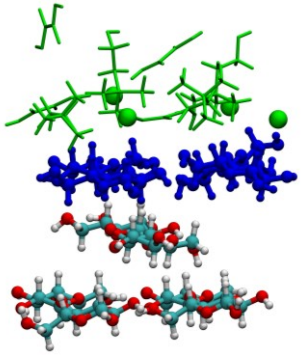
Table S2 and Table S3. The strong non-covalent interactions, i.e., HBs, which correspond to the electronic density values ranging from 0.005 to 0.05 a.u. (Johnson et al. 2010), are indicated in bold. Aditionally, the geometrics for all of the interactions such as hydrogen-acceptor ($H \cdots A$) distance and donor-hydrogen-aceptor ($D - H \cdots A$) angle were also included. On this regard, the HB must have a $D - H \cdots A$ angle between 135° and 180°, and a $H \cdots A$ distance less or equal than 2.5 $\dot{A}$ (Hassan et al. 2021). All the HBs that agreed with both (electronic and geometric) definitions are indicated in bold italics.

Table S2 Obtained interactions between the unit cell located at the top of the cellulose crystallite and close DES molecules, calculated at PBE0/6-311g(d,p) level of theory[a,b,c]

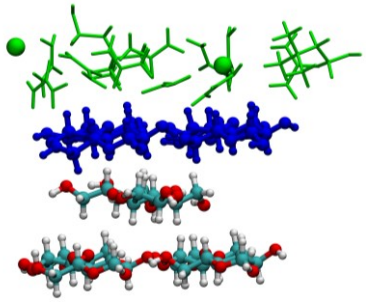
Cellulose-ChCl/ethylene glycol



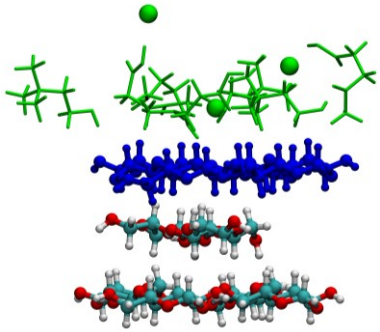
Cellulose-ChCl/oxalic acid



Cellulose-ChCl/urea



Cellulose-ChCl/levulinic acid



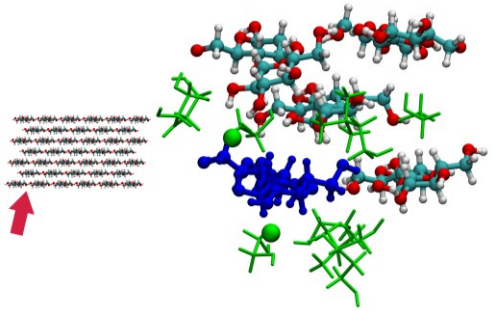
Interaction	$d_{H\cdots A}$ [Å]	$\theta_{D-H\cdots A}$ [degree]	$\rho(\mathbf{r})$ [a.u.]	Interaction	$d_{H\cdots A}$ [Å]	$\theta_{D-H\cdots A}$ [degree]	$\rho(\mathbf{r})$ [a.u.]	Interaction	$d_{H\cdots A}$ [Å]	$\theta_{D-H\cdots A}$ [degree]	$\rho(\mathbf{r})$ [a.u.]	Interaction	$d_{H\cdots A}$ [Å]	$\theta_{D-H\cdots A}$ [degree]	$\rho(\mathbf{r})$ [a.u.]
$O\cdots H-O$	***1.89***	***157.70***	***0.028***	$O-H\cdots Cl$	***2.09***	***168.81***	***0.031***	$O\cdots H-O$	***1.93***	***155.12***	***0.025***	$O-H\cdots O$	***1.93***	***161.01***	***0.025***
$O-H\cdots O$	***2.02***	***160.50***	***0.020***	$O-H\cdots O$	***1.97***	***164.69***	***0.023***	$O\cdots H-C$	***2.34***	***147.26***	***0.012***	$O-H\cdots O$	***2.22***	***160.48***	***0.014***
$O-H\cdots O$	***2.08***	***155.06***	***0.019***	$O-H\cdots Cl$	**2.59**	**154.38**	**0.011**	$N-H\cdots O$	***2.25***	***159.06***	***0.011***	$C-H\cdots O$	***2.35***	***151.71***	***0.012***
$C-H\cdots O$	**2.29**	**133.45**	**0.015**	$C-H\cdots Cl$	**2.95**	**132.48**	**0.007**	$O\cdots H-C$	***2.46***	***138.40***	***0.010***	$O\cdots H-C$	***2.36***	***150.16***	***0.011***
$C-H\cdots O$	***2.48***	***147.71***	***0.010***	$C-H\cdots O$	**2.65**	**147.13**	**0.007**	$O\cdots H-C$	**2.65**	**108.17**	**0.008**	$O\cdots H-C$	***2.41***	***144.70***	***0.010***
$C-H\cdots O$	***2.45***	***161.16***	***0.010***	$C-H\cdots O$	**2.63**	**144.90**	**0.007**	$N-H\cdots O$	**2.53**	**149.32**	**0.007**	$C-H\cdots O$	**2.52**	**135.11**	**0.009**
$C-H\cdots O$	**2.55**	**143.45**	**0.008**	$O\cdots H-C$	**2.73**	**170.59**	**0.006**	$N-H\cdots O$	**2.57**	**163.18**	**0.007**	$C-H\cdots O$	**2.80**	**163.05**	**0.005**
$O\cdots H-C$	**2.61**	**142.96**	**0.008**	$C-H\cdots O$	**2.78**	**111.33**	**0.006**	$O\cdots H-C$	**2.60**	**137.15**	**0.007**	$C-H\cdots O$	2.86	128.68	0.004
$C-H\cdots O$	**2.63**	**134.98**	**0.007**	$C-H\cdots Cl$	**3.15**	**118.31**	**0.006**	$N\cdots H-C$	**2.81**	**126.38**	**0.007**	$O\cdots H-C$	2.91	135.06	0.004
$C-H\cdots O$	**2.76**	**148.26**	**0.006**	$C-H\cdots O$	**2.83**	**120.33**	**0.005**	$N-H\cdots O$	**2.57**	**158.08**	**0.007**	$O\cdots H-C$	3.05	123.55	0.003
$C-H\cdots O$	**2.68**	**153.00**	**0.005**	$C-H\cdots Cl$	**3.08**	**165.37**	**0.005**	$C-H\cdots O$	**2.68**	**126.85**	**0.006**	$O\cdots H-C$	3.08	126.10	0.002
$C-H\cdots Cl$	**3.15**	**142.09**	**0.005**	$O\cdots H-C$	**2.74**	**166.27**	**0.005**	$C-H\cdots Cl$	**3.01**	**160.57**	**0.006**	$O\cdots H-C$	3.30	131.00	0.002
$O\cdots H-C$	**2.82**	**158.50**	**0.005**	$O-H\cdots O$	2.83	136.04	0.004	$N\cdots H-C$	**2.88**	**136.92**	**0.006**	$C-H\cdots O$	3.48	154.19	0.001
$C-H\cdots O$	**2.78**	**170.73**	**0.005**	$C-H\cdots O$	2.91	127.36	0.004	$O\cdots H-C$	**2.80**	**133.83**	**0.005**	$O\cdots H-O$	3.35	139.44	0.001
$O\cdots H-C$	2.94	108.60	0.004	$Cl\cdots H-O$	3.18	155.37	0.004	$N-H\cdots O$	**2.72**	**146.36**	**0.005**	$Cl\cdots H-O$	4.14	164.44	0.001
$O\cdots H-C$	2.89	155.97	0.004	$C-H\cdots O$	2.95	146.48	0.003	$C-H\cdots Cl$	3.21	150.11	0.004	$C-H\cdots O$	3.82	145.16	0.001
$C-H\cdots O$	2.90	142.06	0.004	$O\cdots H-C$	3.10	110.00	0.003	$O\cdots H-C$	2.81	136.25	0.004				
$O\cdots H-C$	2.86	148.04	0.004	$C-H\cdots Cl$	3.32	153.29	0.003	$O\cdots H-C$	2.87	122.99	0.004				
$C-H\cdots O$	3.01	154.42	0.003	$C-H\cdots O$	3.03	130.61	0.003	$N\cdots H-C$	3.03	131.95	0.004				
$C-H\cdots Cl$	3.45	140.00	0.003	$C-H\cdots Cl$	3.51	135.02	0.003	$C\cdots H-C$	3.12	138.41	0.004				
$C-H\cdots Cl$	3.50	167.78	0.003	$O\cdots H-C$	3.34	133.81	0.002	$N\cdots H-C$	3.12	134.56	0.003				
$O\cdots H-C$	3.10	154.95	0.003	$C-H\cdots O$	3.44	138.39	0.001	$N\cdots H-C$	3.13	136.99	0.003				
$C-H\cdots O$	3.21	124.97	0.002	$O\cdots H-C$	3.48	144.77	0.001	$N-H\cdots O$	2.94	138.20	0.003				

$O \cdots H - C$	3.26	150.34	0.002	$O \cdots H - C$	3.52	137.78	0.001	$C - H \cdots O$	3.07	126.38	0.003
$C - H \cdots O$	3.39	139.00	0.002					$O \cdots H - C$	3.05	146.57	0.003
$C - H \cdots Cl$	3.88	148.18	0.001					$O \cdots H - C$	3.08	142.60	0.003
								$N - H \cdots O$	3.04	139.35	0.002
								$N \cdots H - C$	3.30	130.74	0.002
								$N \cdots H - C$	3.31	136.47	0.002
								$N \cdots H - C$	3.33	123.17	0.002
								$N \cdots H - C$	3.40	152.60	0.002
								$N - H \cdots O$	3.15	154.59	0.002
								$N - H \cdots O$	3.24	133.56	0.002
								$O \cdots H - C$	3.36	137.50	0.002

[a] Atoms from DES are indicated in green color, atoms from cellulose unit cell are indicated in blue color.
[b] In bold, hydrogen bonds based on the electronic density definition.
[c] In bold italics, hydrogen bonds based on the geometric definition.

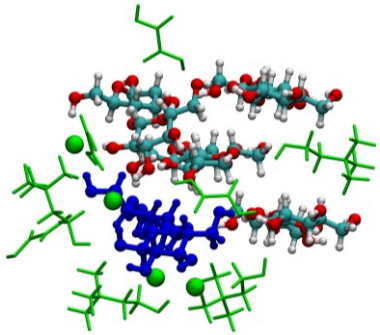
Table S3 Obtained hydrogen bonds between the cellulose unit cell located at the edge of the cellulose crystallite and close DES molecules, calculated at PBE0/6-311g(d,p) level of theory[a,b,c]

Cellulose-ChCl/ethylene glycol



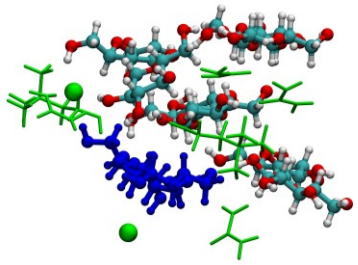
Interaction	$d_{H\cdots A}$ [Å]	$\theta_{D-H\cdots A}$ [degree]	$\rho(\mathbf{r})$ [a.u.]
$O-H\cdots Cl$	***2.11***	***171.03***	***0.031***
$O-H\cdots Cl$	***2.26***	***176.16***	***0.021***
$O\cdots H-C$	**2.30**	**128.08**	**0.014**
$C-H\cdots Cl$	**2.71**	**140.33**	**0.010**
$C-H\cdots O$	**2.48**	**117.66**	**0.010**
$C-H\cdots O$	**2.53**	**125.50**	**0.010**
$C-H\cdots Cl$	**2.77**	**138.44**	**0.010**
$C-H\cdots O$	**2.64**	**141.44**	**0.008**
$C-H\cdots Cl$	**2.88**	**133.29**	**0.008**
$O\cdots H-C$	**2.62**	**141.50**	**0.008**
$O\cdots H-C$	**2.70**	**168.48**	**0.006**
$C-H\cdots Cl$	**2.97**	**132.76**	**0.006**
$C-H\cdots O$	3.00	149.38	0.003
$C-H\cdots O$	3.17	155.69	0.002
$C-H\cdots O$	3.24	132.15	0.002
$C-H\cdots O$	3.21	150.73	0.002

Cellulose-ChCl/oxalic acid



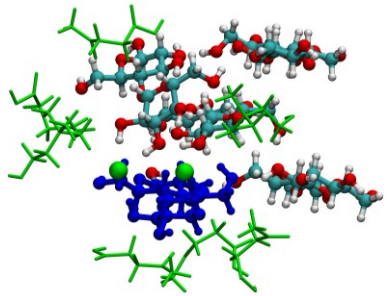
Interaction	$d_{H\cdots A}$ [Å]	$\theta_{D-H\cdots A}$ [degree]	$\rho(\mathbf{r})$ [a.u.]
$O-H\cdots Cl$	***1.90***	***170.20***	***0.050***
$O-H\cdots Cl$	***1.97***	***171.09***	***0.042***
$O-H\cdots Cl$	***2.17***	***163.66***	***0.027***
$O-H\cdots O$	***2.00***	***174.44***	***0.020***
$O-H\cdots O$	***2.14***	***148.78***	***0.016***
$C-H\cdots Cl$	**2.86**	**129.58**	**0.008**
$C-H\cdots O$	**2.66**	**120.13**	**0.008**
$C-H\cdots O$	**2.75**	**137.80**	**0.005**
$C-H\cdots Cl$	**3.12**	**146.50**	**0.005**
$C-H\cdots Cl$	**3.12**	**151.27**	**0.005**
$O-H\cdots Cl$	**3.08**	**130.46**	**0.005**
$O\cdots H-C$	2.93	157.77	0.004
$C-H\cdots O$	2.94	152.52	0.003
$C-H\cdots Cl$	3.34	162.48	0.003
$C-H\cdots O$	2.95	163.00	0.003
$C-H\cdots O$	2.99	154.48	0.003
$C-H\cdots O$	3.31	149.03	0.002
$O\cdots H-C$	3.46	131.46	0.001

Cellulose-ChCl/urea



Interaction	$d_{H\cdots A}$ [Å]	$\theta_{D-H\cdots A}$ [degree]	$\rho(\mathbf{r})$ [a.u.]
$O-H\cdots Cl$	***2.03***	***168.68***	***0.039***
$O-H\cdots Cl$	***2.24***	***170.60***	***0.022***
$O-H\cdots O$	***2.11***	***143.89***	***0.017***
$C-H\cdots O$	**2.29**	**122.26**	**0.016**
$C-H\cdots Cl$	**2.59**	**140.53**	**0.013**
$Cl\cdots H-C$	**2.86**	**131.98**	**0.008**
$O\cdots H-C$	**2.57**	**142.09**	**0.008**
$C-H\cdots O$	**2.61**	**125.55**	**0.008**
$C-H\cdots O$	**2.59**	**119.46**	**0.008**
$O\cdots H-C$	**2.68**	**132.72**	**0.007**
$O\cdots H-C$	**2.81**	**112.52**	**0.006**
$O\cdots H-O$	3.03	151.99	0.002

Cellulose-ChCl/levulinic acid



Interaction	$d_{H\cdots A}$ [Å]	$\theta_{D-H\cdots A}$ [degree]	$\rho(\mathbf{r})$ [a.u.]
$O-H\cdots Cl$	***1.94***	***176.84***	***0.045***
$O-H\cdots Cl$	***2.03***	***155.20***	***0.035***
$C-H\cdots Cl$	**2.66**	**136.32**	**0.011**
$C-H\cdots Cl$	**2.85**	**133.37**	**0.008**
$O\cdots H-C$	**2.47**	**168.82**	**0.008**
$C-H\cdots Cl$	**3.09**	**123.18**	**0.006**
$C-H\cdots O$	**2.81**	**126.33**	**0.005**
$C-H\cdots O$	**2.84**	**120.49**	**0.005**
$C\cdots H-C$	**2.83**	**138.27**	**0.005**
$C-H\cdots O$	2.93	107.41	0.004
$C-H\cdots O$	2.90	127.88	0.004
$C-H\cdots O$	3.46	123.10	0.001
$C-H\cdots O$	3.61	135.24	0.001

[a] Atoms from DES are indicated in green color, atoms from cellulose unit cell are indicated in blue color.
[b] In bold, hydrogen bonds based on the electronic density definition.
[c] In bold italics, hydrogen bonds based on the geometric definition.

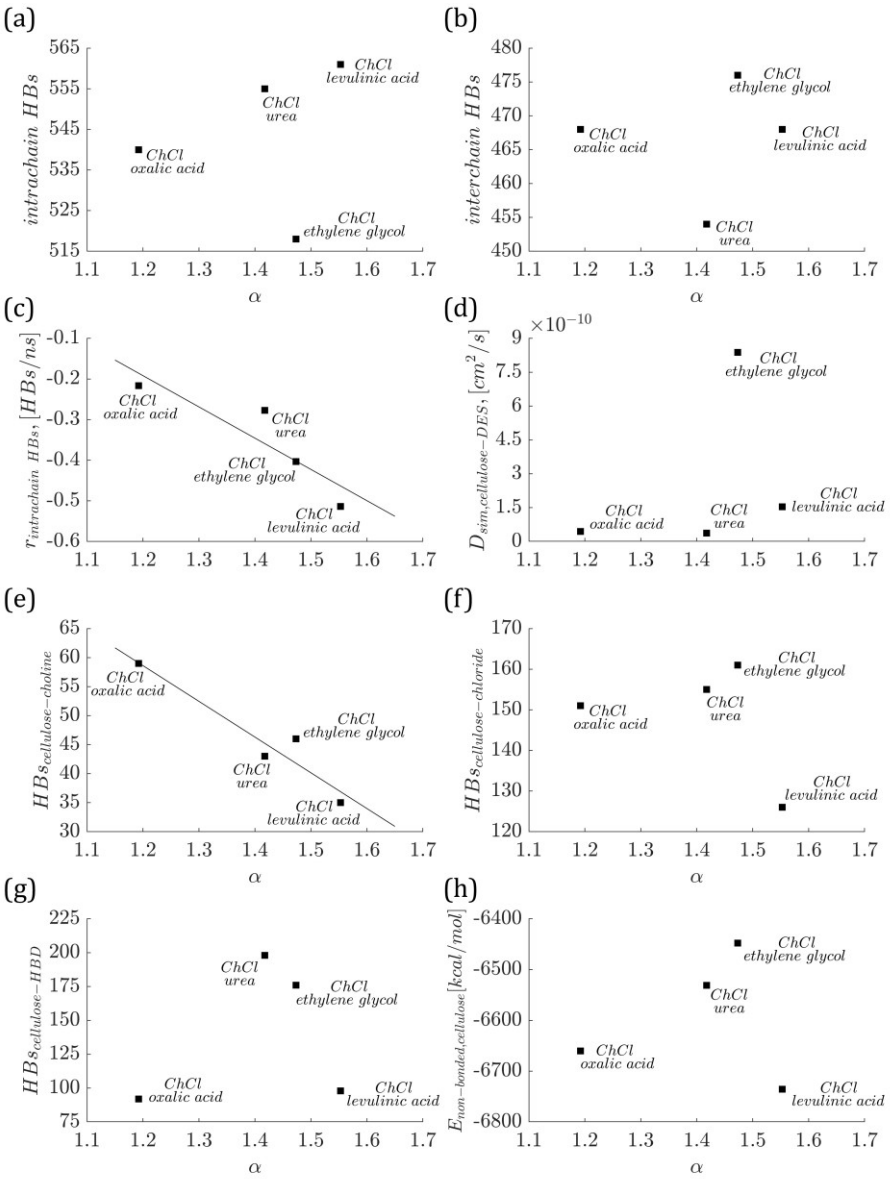


Fig. S13 Linear correlations observed between the Kamlet-Taft α parameter and: **a** Intrachain HBs ($R^2 = 0.038$), **b** Interchain HBs ($R^2 = 0.009$), **c** Rate of change of intrachain HBs ($r_{intrachain\ HBs}$, $R^2 = 0.81$), **d** Cellulose diffusion coefficient in DES ($D_{sim,cellulose-DES}$, $R^2 = 0.14$), **e** HBs between cellulose crystallite and choline cation ($HBs_{cellulose-choline}$, $R^2 = 0.91$), **f** HBs between cellulose crystallite and chloride anion ($HBs_{cellulose-chloride}$, $R^2 = 0.17$), **g** HBs between cellulose crystallite and HBD ($HBs_{cellulose-HBD}$, $R^2 = 0.08$), and **h** Non-bonded potential energy of the cellulose crystallite ($E_{non-bonded,cellulose}$, $R^2 = 0.004$)

***HB occupancies*.** Although this property is often evaluated in biological systems including proteins, (Petukhov et al. 2004) it was found in our previous work (Sánchez-Badillo et al. 2021) that HB occupancies provide relevant information concerning the quality of the cellulose crystallite disruption in ILs. In order to compare two different conditions of the glucan within the cellulose crystallite, the glucan chains located at both the edge and at the middle of the cellulose crystallite were selected to evaluate the HB occupancies. These conditions represented a glucan in direct contact with the solvent (chain 0) and other which was surrounded by other chains (chain 17), as shown in the top of Fig. S14. All the HB occupancies were calculated with the Hydrogen Bonds plugin available in the VMD program (Humphrey et al. 1996), for each glucose unit (namely GLU residue in Fig. S1f) within the chain 0 and the chain 17 for all the cellulose-DES systems over the production period. Calculated intrachain and interchain HB occupancies for cellulose-ChCl/ethylene glycol, cellulose-ChCl/oxalic acid, cellulose-ChCl/urea, and cellulose-ChCl/levulinic acid are shown and Fig. S14, Fig. S15, Fig. S16, and Fig. S17, respectively.

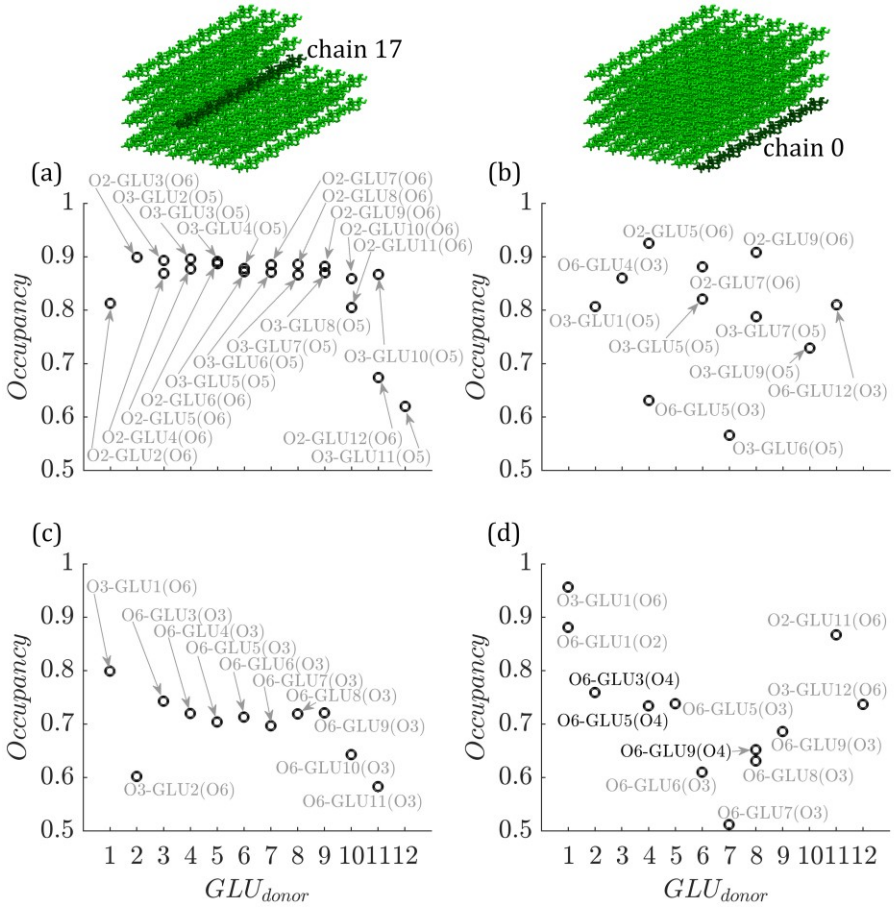


Fig. S14 Calculated cellulose crystallite intrachain and interchain HB occupancies in ChCl/ethylene glycol DES. Intrachain HBs found in **a** Chain 17 and **b** chain 0. Interchain HBs found in **c** chain 17 and **d** chain 0. The hydrogen bond donor atom and the hydrogen bond acceptor atom from glucose units (GLU residues, see Fig. S1f) are plotted along the x-axis and on each point in the graph, respectively. The HB occupancies have been normalized and only HB occupancies higher than 0.5 (50%) are displayed for clarity

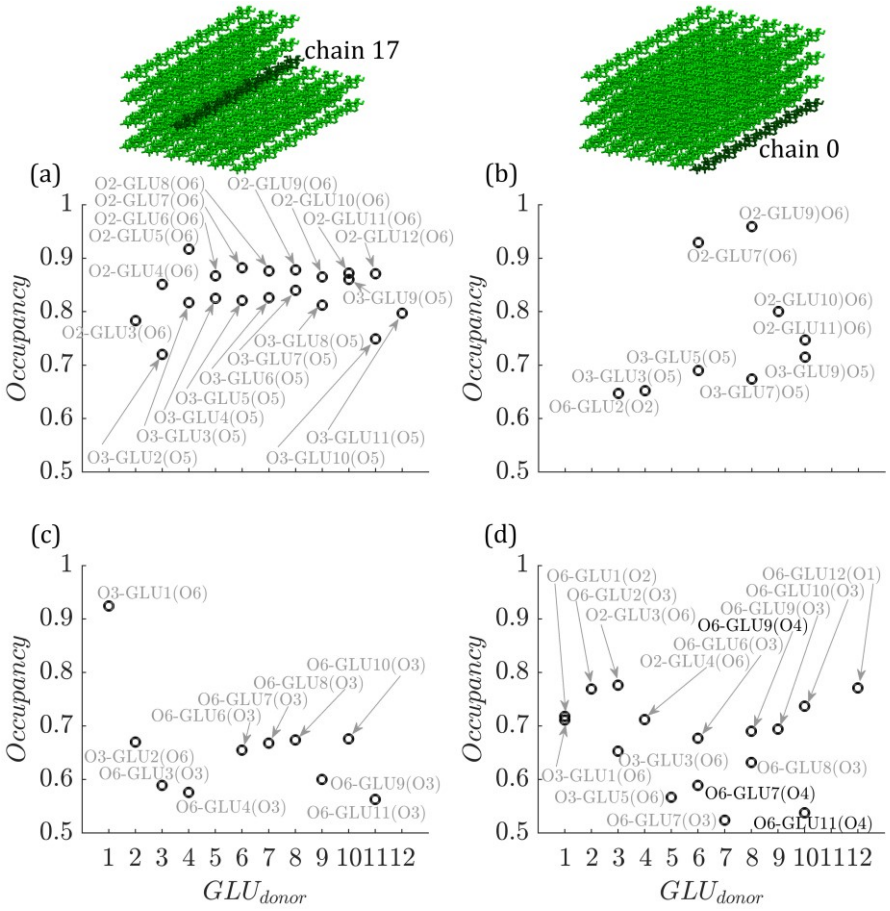


Fig. S15 Calculated cellulose crystallite intrachain and interchain HB occupancies in ChCl/oxalic acid DES. Intrachain HBs found in **a** chain 17 and **b** chain 0. Interchain HBs found in **c** chain 17 and **d** chain 0. The hydrogen bond donor atom and the hydrogen bond acceptor atom from glucose units (GLU residues, see Fig. S1f) are plotted along the x-axis and on each point in the graph, respectively. The HB occupancies have been normalized and only HB occupancies higher than 0.5 (50%) are displayed for clarity

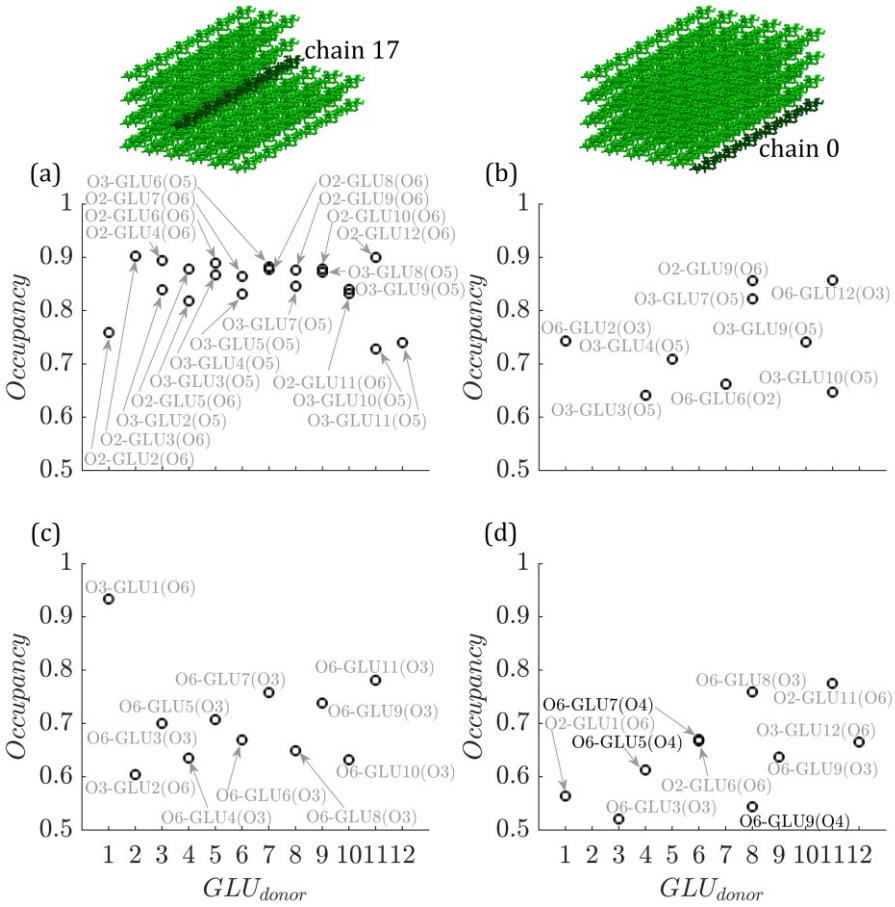


Fig. S16 Calculated cellulose crystallite intrachain and interchain HB occupancies in ChCl/urea DES. Intrachain HBs found in **a** chain 17 and **b** chain 0. Interchain HBs found in **c** chain 17 and **d** chain 0. The hydrogen bond donor atom and the hydrogen bond acceptor atom from glucose units (GLU residues, see Fig. S1f) are plotted along the x-axis and on each point in the graph, respectively. The HB occupancies have been normalized and only HB occupancies higher than 0.5 (50%) are displayed for clarity

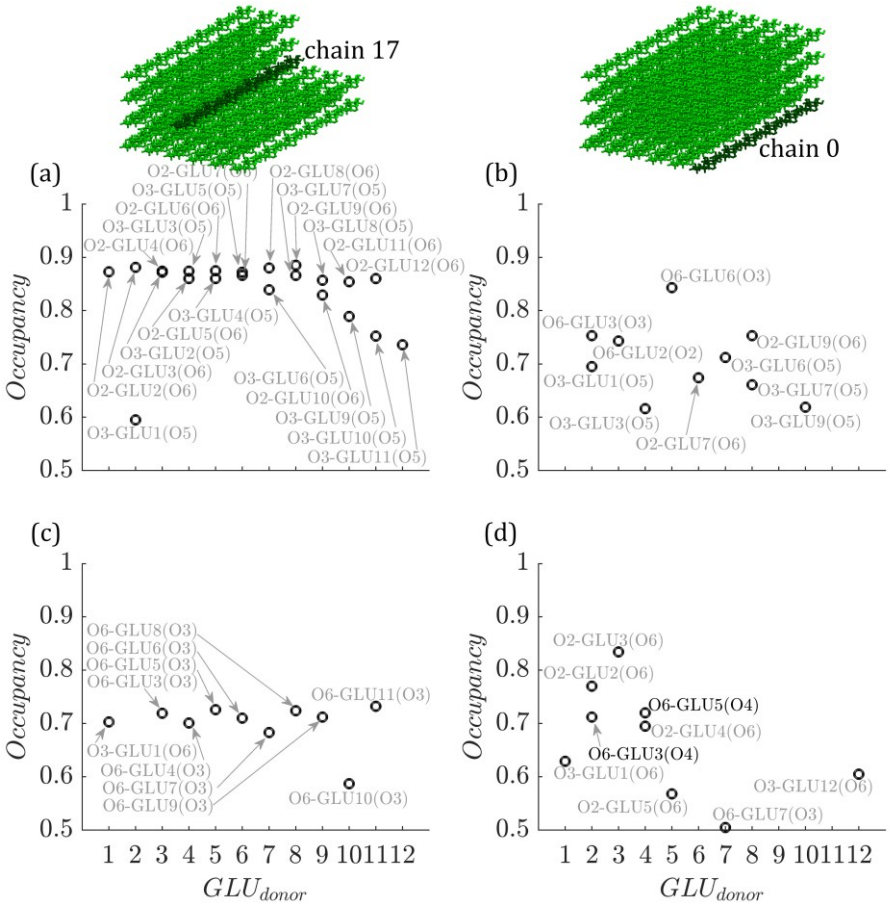


Fig. S17 Calculated cellulose crystallite intrachain and interchain HB occupancies in ChCl/levulinic acid DES. Intrachain HBs found in **a** chain 17 and **b** chain 0. Interchain HBs found in **c** chain 17 and **d** chain 0. The hydrogen bond donor atom and the hydrogen bond acceptor atom from glucose units (GLU residues, see Fig. S1f) are plotted along the x-axis and on each point in the graph, respectively. The HB occupancies have been normalized and only HB occupancies higher than 0.5 (50%) are displayed for clarity

As it can be noted from Fig. S14a-b, S15a-b, S16a-b and S17a-b the intrachain HB occupancies found in both the chain 17 and chain 0 were related to the typical $O2-H2\cdots O6$, $O3-H3\cdots O5$, $O6-H6\cdots O3$, and $O6-H6\cdots O2$ HBs reported in the cellulose Iβ (Shen and Gnanakaran 2009).

The cellulose-ChCl/ethylene glycol system presented the larger occupancies for $O6-H6\cdots O4$ HBs (Fig. S14d), suggesting a large disruption or weakening of the chain 0 from the adjacent chains (more decoupled) as is also shown in Fig. S8. On the other hand, the intrachain HBs for the same glucan 0 (Fig. S14b), indicated that the GLU residues presented some variations in the interactions within the chain, with an average occupancy of ~0.79.

From Fig. S15d, the cellulose-ChCl/oxalic acid system also presented three HB occupancies related to the $O6-H6\cdots O4$ interaction with an occupancy of ~0.61 for them. Despite this advantage, the system also shows a larger number of intrachain HB occupancies favoring the compactness of the cellulose crystallite, compared to the cellulose-ChCl/ethylene glycol system, as is displayed in Fig. S9. Additionally, the intrachain HB occupancies were biased to lower values (~0.70) as can be noticed in Fig.

S15b. This suggested that the glucan chains within the cellulose crystallite model were not disrupted, but the intrachain HBs were, as indicated in Table 4. This effect could be related to a larger effect of weak interactions from the choline cation over both chloride anion and oxalic acid HBD towards the cellulose, as suggested by the RDF analysis (Table 3). These observations agreed with the larger value for the $E_{non-bonded,cellulose}$ computed for the cellulose-ChCl/oxalic acid system of -6660.10 kcal/mol; i.e., a more stable (less disrupted) cellulose crystallite than the one in the cellulose-ChCl/ethylene glycol system.

In the cellulose-ChCl/urea system (Fig. S16d), the small interchain HB occupancies and the three weak $O6-H6\cdots O4$ HBs suggested that the chain 0 is disrupting from the adjacent chains, as shown in Fig. S10. Despite interchain HBs ranged from ~0.6 to ~0.85, the small $OC-HY$ and $HS-Cl$ distances shown in Table 3, and the large number of the $HBs_{cellulose-HBD}$, indicated a major role of the DES in this system. In addition, the $E_{non-bonded,cellulose}$ computed with the cellulose crystallite shown in Fig. S10a gave a value of -6530.86 kcal/mol, in agreement with both the $E_{non-bonded,cellulose}$ and the Kamlet-Taft β and α values of the ChCl/oxalic acid, ChCl/urea, and ChCl/ethylene glycol DESs.

Finally, the interchain HB occupancies from the cellulose crystallite in ChCl/levulinic acid DES (Fig. S17d), presented only two large $O6-H6\cdots O4$ HB occupancies (~0.71). As is observed from the same figure, this system showed large occupancies for the GLU1 to GLU5 and GLU12 residues, whereas large HB occupancy values were not observed (less than 0.5) for the remaining GLU residues. Additionally, from Fig. S17b, the intrachain HB occupancies appeared in a narrow region with average occupancy of ~0.71. The largest Kamlet-Taft β parameter for the ChCl/levulinic acid DES (0.61) (Kundu et al. 2020) would suggest a large cellulose disruption, although the largest (less disrupted crystallite) value of -6735.63 kcal/mol for the $E_{non-bonded,cellulose}$ was obtained for this system.

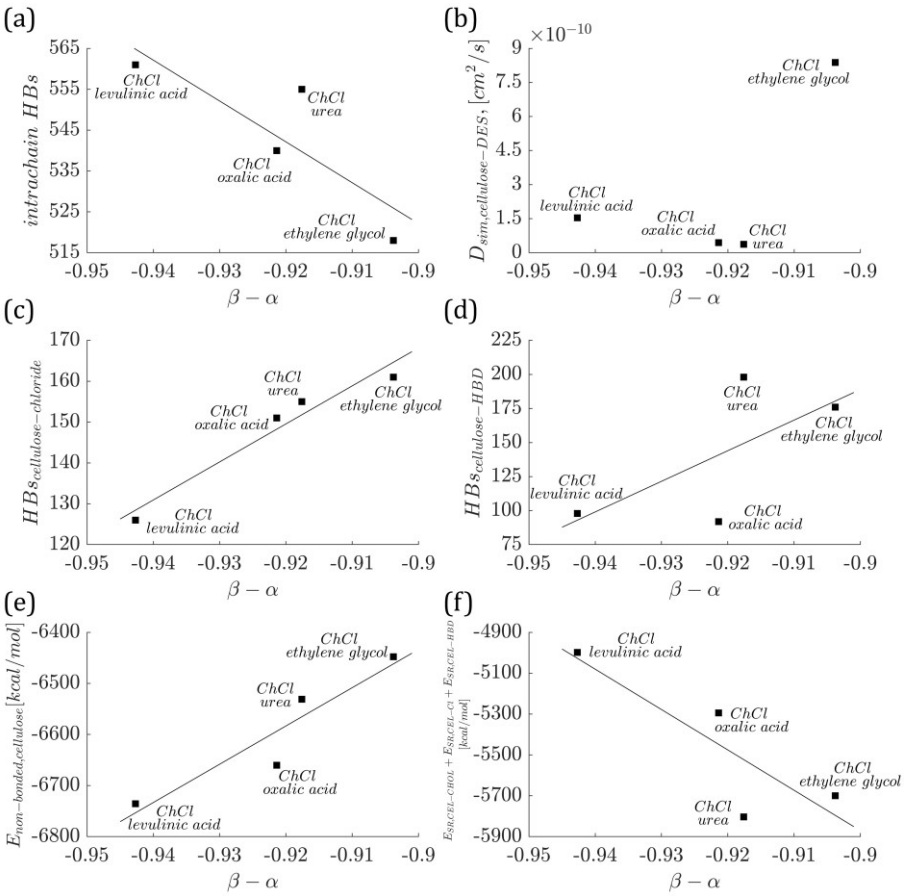


Fig. S18 Linear correlations observed between the neat basicity $\beta - \alpha$ and: **a** Intrachain HBs ($R^2 = 0.71$), **b** Cellulose diffusion coefficient in DES ($D_{sim,cellulose-DES}$, $R^2 = 0.39$), **c** HBs between cellulose crystallite and chloride anion ($HBs_{cellulose-chloride}$, $R^2 = 0.95$), **d** HBs between cellulose crystallite and HBD ($HBs_{cellulose-HBD}$, $R^2 = 0.45$), **e** Non-bonded potential energy of the cellulose crystallite ($E_{non-bonded,cellulose}$, $R^2 = 0.88$), and **f** Non-bonded energy contributions ($E_{SR,CEL-CHOL} + E_{SR,CEL-Cl} + E_{SR,CEL-HBD}$, $R^2 = 0.73$)

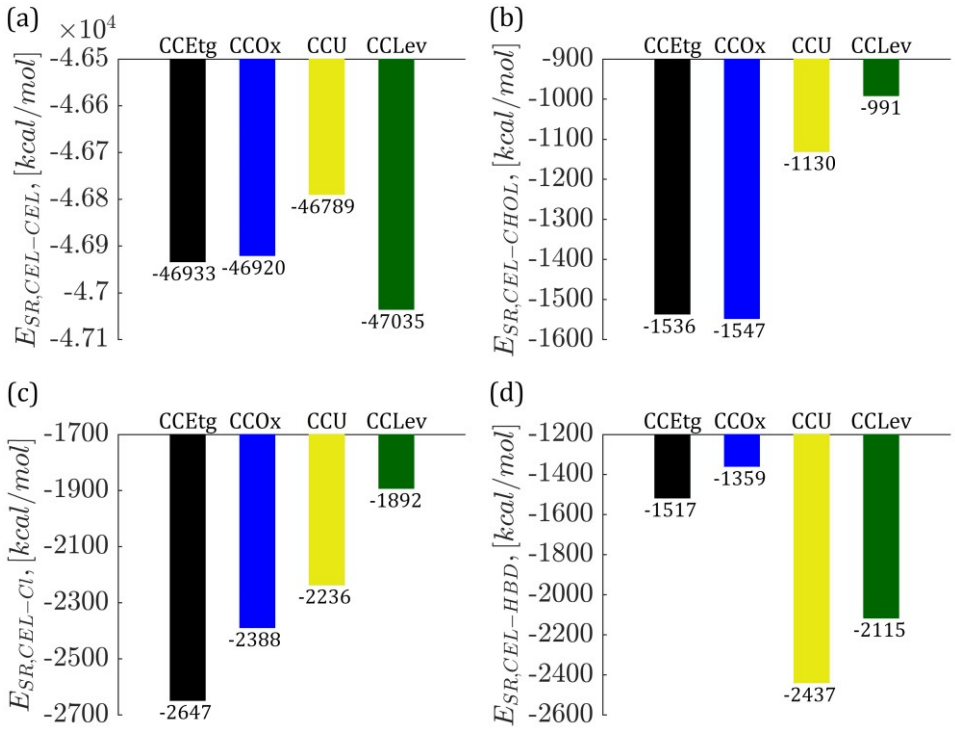


Fig. S19 Calculated non-bonded pair energies (E_{SR}) for: **a** Cellulose crystallite ($E_{SR,CEL-CEL}$), **b** Cellulose crystallite and choline cation ($E_{SR,CEL-CHOL}$), **c** Cellulose crystallite and chloride anion ($E_{SR,CEL-Cl}$), and **d** Cellulose crystallite and HBD ($E_{SR,CEL-HBD}$) in cellulose-ChCl/ethylene glycol (black bar), cellulose-ChCl/oxalic acid (blue bar), cellulose-ChCl/urea (yellow bar), and cellulose-ChCl/levulinic acid (green bar) systems.

References

Adamo C, Barone V (1999) Toward reliable density functional methods without adjustable parameters: The PBE0 model. J Chem Phys 110:6158-6169. http://doi.org/10.1063/1.478522

Contreras-García J, Yang W, Johnson ER (2011) Analysis of hydrogen-bond interaction potentials from the electron density: Integration of noncovalent interaction regions. J Phys Chem A 115:12983-12990. http://doi.org/10.1021/jp204278k

Cruz JC, Hernández-Esparza R, Vázquez-Mayagoitia Á, Vargas R, Garza J (2019) Implementation of the molecular electrostatic potential over graphics processing. J Chem Inf Model 59:3120-3127. http://doi.org/10.1021/acs.jcim.8b00951

Dennington R, Keith TA, Millam JM (2016) GaussView, Version 6. Shawnee Mission, KS: Semichem Inc.

Grimme S, Antony J, Ehrlich S, Krieg H (2010) A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J Chem Phys 132:154104. http://doi.org/10.1063/1.3382344

Hassan I, Ferraro F, Imhof P (2021) Effect of the hydration shell on the carbonyl vibration in the Ala-Leu-Ala-Leu peptide. Molecules 26:2148. https://doi.org/10.3390/molecules26082148

Hernández-Esparza R, Mejía-Chica S-M, Zapata-Escobar AD, Guevara-García A, Martínez-Melchor A, Hernández-Pérez J-M, Vargas R, Garza J (2014) Grid-based algorithm to search critical points, in the electron density, accelerated by graphics processing units. J Comput Chem 35:2272-2278. http://doi.org/10.1002/jcc.23752

Hernández-Esparza R, Vázquez-Mayagoitia Á, Soriano-Agueda L-A, Vargas R, Garza J (2019) GPUs as boosters to analyze scalar and vector fields in quantum chemistry. Int J Quantum Chem 119:e25671. http://doi.org/10.1002/qua.25671

Humphrey W, Dalke A, Schulten K (1996) VMD: Visual molecular dynamics. J Mol Graphics 14:33-38. https://doi.org/10.1016/0263-7855(96)00018-5

Johnson ER, Keinan S, Mori-Sánchez P, Contreras-García J, Cohen AJ, Yang W (2010) Revealing noncovalent interactions. J Am Chem Soc 132:6498-6506. https://doi.org/10.1021/ja100936w

Kundu D, Rao PS, Banerjee T (2020) First principle prediction of Kamlet-Taft solvatochromic parameters of deep eutectic solvent using COSMO-RS model. Ind Eng Chem Res 59:11329-11339. https://doi.org/10.1021/acs.iecr.0c00574

Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Phys Rev Lett 77:3865-3868. http://doi.org/10.1103/PhysRevLett.77.3865

Perdew JP, Burke K, Ernzerhof M (1997) Generalized gradient approximation made simple. Phys Rev Lett 78:1396. http://doi.org/10.1103/PhysRevLett.78.1396

Petukhov M, Rychkov G, Firsov L, Serrano L (2004) H-bonding in protein hydration revisited. Protein Science 13:2120-2129. http://doi.org/10.1110/ps.04748404

Sánchez-Badillo JA, Gallo M, Rutiaga-Quiñones JG, López-Albarrán P (2021) Solvent behavior of an ionic liquids set around a cellulose Iβ crystallite model through molecular dynamics simulations. Cellulose 28:6767-6795. https://doi.org/10.1007/s10570-021-03992-7

Shen T, Gnanakaran S (2009) The stability of cellulose: A statistical perspective from a coarse-grained model of hydrogen-bond networks. Biophys J 96:3032-3040. https://doi.org/10.1016/j.bpj.2008.12.3953

Ufimtsev IS, Martínez TJ (2008) Quantum chemistry on graphical processing units. 1. Strategies for two-electron integral evaluation. J. Chem. Theory Comput. 4:222-231. http://doi.org/10.1021/ct700268q

Zou W *Molden2Aim, Version 4.3.0* [Online]. Available: https://github.com/zorkzou/Molden2AIM [Accessed 26 Oct 2021]