Electronic Supplementary Material (ESI) for Green Chemistry.

Practical guide to designing safer ionic liquids for cellulose dissolution using a tiered computational framework

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SUPPLEMENTARY INFORMATION

Table S1. Electrostatic (Coulomb, Coul) and van der Waals (Lennard Jones, LJ) interactions computed between selected ionic liquids (ILs) and glucose from PM7/OPLS-AA/MC simulations as well as between glucose and glucose, using scaled CM3 charges. All energies are reported in kcal/mol. "IL" = IL pair used as solute; "CAT" = IL cation used as solute; "AN" = IL anion used as solute; "SOL" = apparent exptl. solubility values (obtained from Ref 20). Calculated coefficients of determination, R^2, are reported below solute-solvent/solvent-solvent energetics for each species. IL name abbreviations correspond to Table 2 in the main text.

	SOL (wt%)	SOL (g/mol)	Coul	LJ	# weak	# strong	
EmimAc	27	46	-68.82	-19.81	8.53	6.83	**CAT**
AmimCl	<17	<26	-63.57	-22.58	6.59	5.27	
EmimDEP	15	40	-68.82	-19.81	8.53	6.83	
ApyCl	15	23	-69.30	-22.08	7.53	6.71	
HOEtmimBr	9.1	19	-76.67	-20.87	7.63	6.05	
HOEtpyBr	9.1	18	-79.42	-21.60	9.84	8.03	
EtOMmiomCl	8.3	15	-68.20	-25.02	7.53	5.82	
R^2			**0.23**	**0.57**	**0.04**	**0.03**	
EmimAc	27	46	-93.91	-8.83	7.79	7.34	**AN**
AmimCl	<17	<26	-108.89	-1.40	5.30	4.25	
EmimDEP	15	40	-87.95	-24.57	6.41	4.60	
ApyCl	15	23	-108.89	-1.40	5.30	4.25	
HOEtmimBr	9.1	19	-101.08	-0.57	3.79	2.34	
HOEtpyBr	9.1	18	-101.08	-0.57	3.79	2.34	
EtOMmiomCl	8.3	15	-108.89	-1.40	5.30	4.25	
R^2			**0.66**	**0.56**	**0.77**	**0.65**	
EmimAc	27	46	-135.03	-17.61	4.45	3.28	**IL**
AmimCl	<17	<26	-135.59	-5.62	1.25	1.10	
EmimDEP	15	40	-134.41	-15.03	1.98	1.26	
ApyCl	15	23	-143.85	-7.71	4.13	3.20	
HOEtmimBr	9.1	19	-165.15	-5.61	4.82	3.80	
HOEtpyBr	9.1	18	-134.78	-9.77	4.16	3.37	
EtOMmiomCl	8.3	15	-168.03	-7.04	3.81	2.72	
R^2			**0.43**	**0.89**	**0.14**	**0.18**	

			Coul	LJ	Total	Coul	GLU-GLU
EmimAc	27	46	-4004.6	-2780.2	-6784.8	-4004.6	
AmimCl	<17	<26	-4083.6	-2790.6	-6874.2	-4083.6	
EmimDEP	15	40	-4041.8	-2693.3	-6735.1	-4041.8	
ApyCl	15	23	-4152.4	-2791.9	-6944.3	-4152.4	
HOEtmimBr	9.1	19	-4218.8	-2740.4	-6959.2	-4218.8	
HOEtpyBr	9.1	18	-4266.2	-2755.3	-7021.5	-4266.2	
EtOMmiomCl	8.3	15	-4091.5	-2781.3	-6872.9	-	
R^2			**0.60**	**0.08**	**0.66**	**0.95**	

Table S2. Physicochemical properties calculated or predicted from QM/MM/MC simulations in BOSS 4.9 and corresponding coefficients of determination, R^2, with computed Lennard Jones interaction energies in kcal/mol, ΔE_{LJ}, between ILs and glucose medium. MW = molecular weight, SASA = solvent accessible surface area (Å^2), FOSA = hydrophobic SASA, FISA = hydrophilic SASA, PISA = Π-carbon SASA, WPSA = weakly polar SASA, donorHB = solute as hydrogen-bond donor, accptHB = solute as hydrogen-bond acceptor, dip^2/V = dipole^2/volume, glob = globularity, polrz = polarizability (Å^3), logPC16 = log P for hexadecane/gas, logPoct = log P for octanol/gas, logPw = log P for water/gas, logPo/w = log P for octanol/water, logSw = aqueous solubility.

	ΔE_{LJ}	MW	dipole	SASA	FOSA	FISA
EmimAc	-17.61	170.21	17.12	433.95	253.11	49.23
AmimCl	-5.62	158.63	15.43	592.74	286.14	0.00
EmimDEP	-15.03	264.26	16.10	401.43	268.65	26.05
ApyCl	-7.706	155.63	15.95	500.29	151.29	0.00
HOEtmimBr	-5.612	207.07	18.37	552.59	211.79	76.21
HOEtpyBr	-9.774	204.07	17.97	380.19	24.54	59.55
EtOMmiomCl	-7.038	176.65	16.01	652.26	386.77	0.00
34MpyC4BR	-11.75	244.17	18.65	316.27	131.52	0.00
C2mimNO3	-10.9	173.17	20.90	513.20	203.46	154.02
C4mimBr	-9.241	219.12	27.27	529.46	243.10	0.28
C4mimCl	-7.938	174.67	24.26	503.32	240.53	0.28
C4mimNO3	-9.88	201.23	23.86	449.64	135.33	185.86
ChAla	-12.82	192.26	28.80	681.74	386.30	295.44
ChGly	-5.708	164.20	34.22	719.70	337.53	382.18
ChLeu	-18.32	234.34	44.80	578.01	360.35	217.66
ChSer	-16.58	208.26	45.54	738.49	352.48	386.01
ChVal	-17.12	220.31	40.50	702.71	406.31	296.40
C4pyBr	n.a.	216.12	18.12	319.27	16.60	0.31
2CAm2CNCO2	-4.177	134.18	23.49	626.67	465.57	161.10
35MpyC4Br	-21.71	244.17	24.07	394.46	186.03	0.37

3MpyC4Br	-17.31	230.15	18.03	351.19	118.37	0.32
3MpyC6Br	-11.66	258.20	34.29	477.80	102.72	0.37
4C4AmBr	-24.6	322.37	25.42	246.49	150.01	0.00
4C4PhosBr	-24.15	339.34	52.95	278.06	62.45	0.00
C2mimOTs	-17.43	282.36	23.67	694.83	303.78	163.14
C4pyrrTf2N	-37.58	422.40	25.12	536.81	91.08	136.99
C6mimBr	-7.019	247.18	36.23	475.61	94.14	0.22
C6mimCl	-10.6	202.73	34.33	469.64	97.41	0.20
C6mimNO3	-23.79	229.28	24.33	473.98	132.35	209.80
C4pyCl	-7.88	171.67	31.05	400.00	15.93	0.37
C4pyTf2N	-38.17	416.35	27.20	595.30	33.96	112.46
R^2		**0.76**	**0.04**	**0.02**	**0.10**	**0.01**

	dELJ	**PISA**	**WPSA**	**volume**	**donorHB**	**accptHB**	**dip^2/V**
EmimAc	-17.61	131.61	0.00	1272.26	0.00	4.89	0.23
AmimCl	-5.62	203.62	102.98	1428.23	0.00	0.00	0.17
EmimDEP	-15.03	106.72	0.00	1491.36	0.00	4.83	0.17
ApyCl	-7.706	231.07	117.94	1269.25	0.00	0.00	0.20
HOEtmimBr	-5.612	136.63	127.96	1352.08	0.37	0.36	0.25
HOEtpyBr	-9.774	182.51	113.58	1070.87	0.89	0.86	0.30
EtOMmiomCl	-7.038	145.83	119.66	1570.15	0.00	1.10	0.16
34MpyC4BR	-11.75	59.30	125.45	1189.63	0.00	0.00	0.29
C2mimNO3	-10.9	155.73	0.00	1345.44	0.00	6.98	0.32
C4mimBr	-9.241	130.21	155.87	1439.96	0.00	0.05	0.52
C4mimCl	-7.938	129.09	133.42	1382.88	0.00	0.00	0.43
C4mimNO3	-9.88	128.45	0.00	1391.50	0.00	8.43	0.41
ChAla	-12.82	0.00	0.00	1768.46	2.75	4.73	0.47
ChGly	-5.708	0.00	0.00	1734.70	2.51	10.02	0.68
ChLeu	-18.32	0.00	0.00	1755.51	1.21	8.48	1.14
ChSer	-16.58	0.00	0.00	1850.77	2.70	6.40	1.12
ChVal	-17.12	0.00	0.00	1975.53	1.16	6.52	0.83
C4pyBr	n.a.	193.08	109.29	1071.82	0.00	0.01	0.31
2CAm2CNCO2	-4.177	0.00	0.00	1441.66	2.74	5.41	0.38
35MpyC4Br	-21.71	76.39	131.68	1360.20	0.00	0.00	0.43
3MpyC4Br	-17.31	133.49	99.01	1182.00	0.00	0.00	0.27
3MpyC6Br	-11.66	161.66	213.04	1586.85	0.00	0.00	0.74
4C4AmBr	-24.6	0.00	96.49	1529.95	0.00	0.00	0.42
4C4PhosBr	-24.15	0.00	215.61	1692.18	0.00	0.00	1.66
C2mimOTs	-17.43	227.23	0.68	1886.63	0.00	5.61	0.30
C4pyrrTf2N	-37.58	0.00	308.74	1900.53	0.00	2.41	0.33

C6mimBr	-7.019	175.60	205.65	1487.90	0.00	0.01	0.88
C6mimCl	-10.6	177.51	194.52	1468.81	0.00	0.00	0.80
C6mimNO3	-23.79	131.83	0.00	1536.72	0.00	8.34	0.39
C4pyCl	-7.88	185.53	198.17	1223.57	0.00	0.00	0.79
C4pyTf2N	-38.17	134.18	314.70	1935.70	0.00	3.85	0.38
R²		**0.11**	**0.12**	**0.26**	**0.04**	**0.01**	**0.01**

	dELJ	**glob**	**polrz**	**logPC16**	**logPoct**	**logPw**	**logPo/w**	**logSw**
EmimAc	-17.61	1.31	21.22	14.98	23.97	45.35	-1.31	-1.88
AmimCl	-5.62	1.03	20.92	17.74	30.09	59.26	4.60	-1.07
EmimDEP	-15.03	1.57	29.76	12.27	29.08	50.77	0.76	-1.11
ApyCl	-7.706	1.13	20.08	16.80	28.43	56.12	4.22	-1.77
HOEtmimBr	-5.612	1.07	18.30	16.04	28.96	56.17	3.29	-0.17
HOEtpyBr	-9.774	1.33	19.44	35.90	36.16	72.26	3.76	-1.46
EtOMmiomCl	-7.038	1.00	19.00	12.78	26.01	51.29	3.43	-0.24
34MpyC4BR	-11.75	1.72	24.77	11.83	24.88	44.44	5.35	-3.12
C2mimNO3	-10.9	1.15	22.06	23.40	29.83	55.22	-2.27	-0.51
C4mimBr	-9.241	1.16	23.17	19.35	30.26	57.70	5.27	-1.37
C4mimCl	-7.938	1.19	23.84	17.40	29.33	55.22	5.31	-0.98
C4mimNO3	-9.88	1.34	25.01	18.28	28.72	50.25	-1.38	0.43
ChAla	-12.82	1.04	22.45	24.70	36.66	71.25	-3.70	-1.97
ChGly	-5.708	0.97	20.75	23.24	36.93	69.18	-3.08	1.11
ChLeu	-18.32	1.22	27.35	41.07	44.00	87.55	-2.37	-2.66
ChSer	-16.58	0.99	22.95	43.11	43.09	86.50	-3.80	-2.77
ChVal	-17.12	1.08	27.30	39.83	44.36	87.23	-2.65	-2.33
C4pyBr	n.a.	1.59	22.66	28.38	33.58	66.23	5.00	n.a.
2CAm2CNCO2	-4.177	0.98	17.15	17.03	29.86	57.52	-2.04	0.63
35MpyC4Br	-21.71	1.51	26.62	16.55	28.61	51.83	5.86	-5.23
3MpyC4Br	-17.31	1.54	24.58	28.81	34.32	67.03	5.40	-3.87
3MpyC6Br	-11.66	1.38	30.12	20.71	33.57	59.90	6.96	-2.13
4C4AmBr	-24.6	2.61	32.26	16.11	30.58	50.88	7.73	-7.42
4C4PhosBr	-24.15	2.47	36.50	32.51	44.79	81.49	9.02	-7.27
C2mimOTs	-17.43	1.06	31.76	16.21	27.85	49.63	0.06	-1.51
C4pyrrTf2N	-37.58	1.38	34.09	16.45	27.00	43.77	2.41	-9.09
C6mimBr	-7.019	1.33	26.58	22.58	33.49	62.36	6.22	-0.70
C6mimCl	-10.6	1.33	26.35	22.08	34.26	64.30	6.20	-1.80
C6mimNO3	-23.79	1.36	28.47	17.89	29.16	48.02	-0.21	-3.90
C4pyCl	-7.88	1.38	22.90	20.47	31.02	59.62	5.11	-0.97
C4pyTf2N	-38.17	1.26	36.21	22.71	31.17	51.44	2.86	-8.65
R²		**0.17**	**0.65**	**0.01**	**0.01**	**0.01**	**0.00**	**0.85**

Table S3. Physicochemical properties calculated and predicted for side chain (R groups) in the IL set by Liu et al. using QikProp 2.2. Corresponding coefficients of determination, R^2, are provided for univariate correlations with computed Lennard Jones interaction energies in kcal/mol, ΔE_{LJ}, between ILs and glucose medium. MW = molecular weight, SASA = solvent accessible surface area (Å^2), FOSA = hydrophobic SASA, FISA = hydrophilic SASA, PISA = Π-carbon SASA, WPSA = weakly polar SASA, donorHB = solute as hydrogen-bond donor, accptHB = solute as hydrogen-bond acceptor, dip^2/V = dipole^2/volume, glob = globularity, polrz = polarizability (Å^3), logPC16 = log P for hexadecane/gas, logPoct = log P for octanol/gas, logPw = log P for water/gas, logPo/w = log P for octanol/water, logSw = aqueous solubility, CIlogSw = conformation-independent aqueous solubility, IP = ionization potential, EA = electron affinity.

IL	EmimAc	AmimCl	EmimDEP	ApyCl	HOEtmimBr	HOEtpyBr	EtOMmiomCl	R^2
MW	30.07	56.11	30.07	56.11	46.07	46.07	60.10	**0.11**
dipole	0.00	0.29	0.00	0.29	2.03	2.03	1.54	**0.29**
SASA	202.39	258.46	202.39	258.46	215.20	215.20	246.85	**0.53**
FOSA	202.39	214.09	202.39	214.09	158.99	158.99	246.85	**0.00**
FISA	0.00	0.00	0.00	0.00	56.20	56.20	0.00	**0.09**
PISA	0.00	44.37	0.00	44.37	0.00	0.00	0.00	**0.20**
WPSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**n.a.**
volume	256.84	360.93	256.84	360.93	280.12	280.12	341.06	**0.52**
donorHB	0.00	0.00	0.00	0.00	1.00	1.00	0.00	**0.09**
accptHB	0.00	0.00	0.00	0.00	1.70	1.70	1.70	**0.20**
dip^2/V	0.00	0.00	0.00	0.00	0.01	0.01	0.01	**0.17**
glob	0.97	0.95	0.97	0.95	0.96	0.96	0.96	**0.47**
polrz	4.13	8.07	4.13	8.07	4.41	4.41	6.85	**0.39**
logPC16	0.51	1.91	0.51	1.91	1.39	1.39	1.46	**0.81**
logPoct	-0.02	1.35	-0.02	1.35	2.89	2.89	1.88	**0.57**
logPw	-1.38	-1.12	-1.38	-1.12	3.54	3.54	1.77	**0.21**
logPo/w	1.81	1.94	1.81	1.94	-0.31	-0.31	0.21	**0.16**
logSw	-1.36	-1.79	-1.36	-1.79	1.04	1.04	0.54	**0.11**
CIlogSw	-1.36	-1.57	-1.36	-1.57	0.04	0.04	0.09	**0.13**
IP(eV)	11.97	10.15	11.97	10.15	10.90	10.90	10.57	**0.81**
EA(eV)	-3.89	-1.18	-3.89	-1.18	-3.34	-3.34	-3.02	**0.42**

Table S4. ILs ordered by increasing solubility in octanol, log S_o = log S_w + log $P_{o/w}$.

	log S_w	log $P_{o/w}$	log S_w + log $P_{o/w}$
C4pyrrTf2N	-9.09	2.41	-6.68
ChSer	-2.77	-3.80	-6.57
C4pyTf2N	-8.65	2.86	-5.79
ChAla	-1.97	-3.70	-5.66
ChLeu	-2.66	-2.37	-5.03
ChVal	-2.33	-2.65	-4.98
C6mimNO3	-3.90	-0.21	-4.11
EmimAc	-1.88	-1.31	-3.19
C2mimNO3	-0.51	-2.27	-2.78
ChGly	1.11	-3.08	-1.97
C2mimOTs	-1.51	0.06	-1.46
2CAm2CNCO2	0.63	-2.04	-1.42
C4mimNO3	0.43	-1.38	-0.96
EmimDEP	-1.11	0.76	-0.35
4C4AmBr	-7.42	7.73	0.31
35MpyC4Br	-5.23	5.86	0.63
3MpyC4Br	-3.87	5.40	1.53
4C4PhosBr	-7.27	9.02	1.75
34MpyC4BR	-3.12	5.35	2.23
HOEtpyBr	-1.46	3.76	2.30
ApyCl	-1.77	4.22	2.44
HOEtmimBr	-0.17	3.29	3.13
EtOMmiomCl	-0.24	3.43	3.19
AmimCl	-1.07	4.60	3.53
C4mimBr	-1.37	5.27	3.90
C4pyCl	-0.97	5.11	4.15
C4mimCl	-0.98	5.31	4.33
C6mimCl	-1.80	6.20	4.40
3MpyC6Br	-2.13	6.96	4.82
C4pyBr	n.a.	5.00	n.a.
C6mimBr	-0.70	6.22	5.52

Figure S1. IL cations and anions explored in this study with corresponding abbreviations.