Supporting Information

Solvatochromic parameters of deep eutectic solvents: effect of different carboxylic acids as hydrogen bond donor

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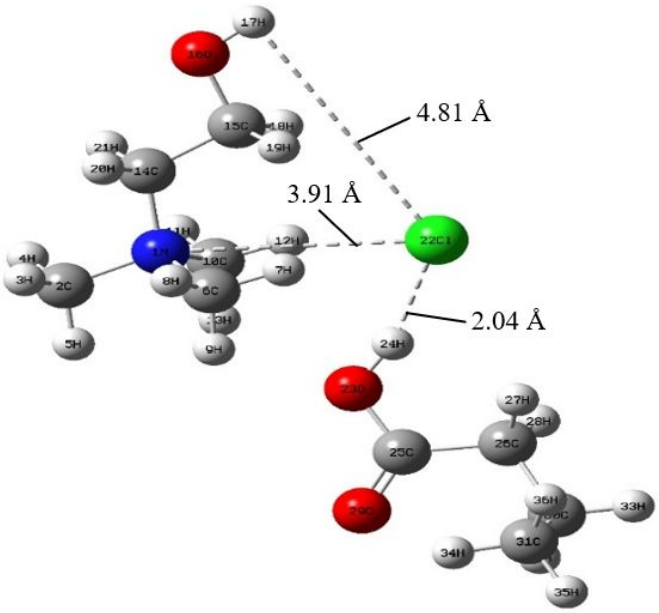
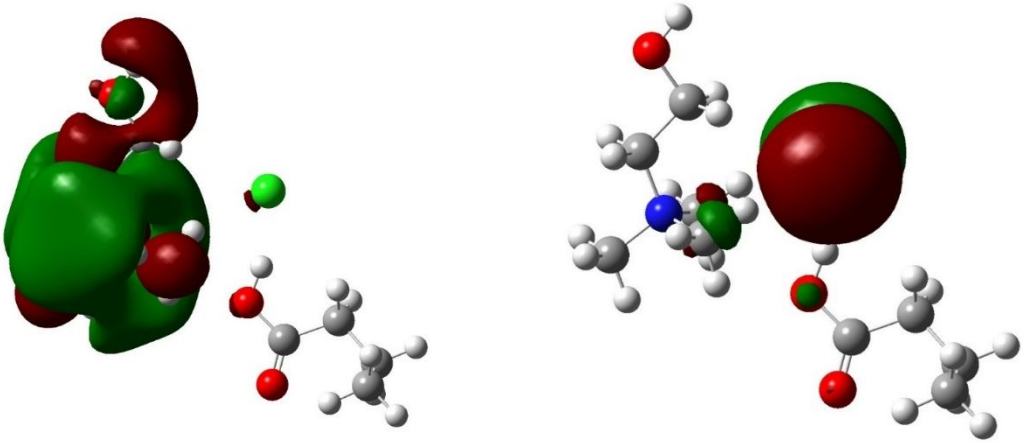


Fig. S1. Optimized equilibrium geometry structure of [Ch]Cl:BA (1:1) DES. Atoms are colored according to type: C (gray), O (red), N (blue), H (white), and Cl (light green). Bond angle between C14-C15-O16 (102.69 º), C15-O16-H17 (107.40 º), C2-N1-C14 (107.94 º), and N1-C14-C15 (116.54 º).



a) **b)**

Fig. S2. Frontier molecular orbitals of [Ch]Cl:BA (1:1) DES: (a) HOMO and (b) LUMO

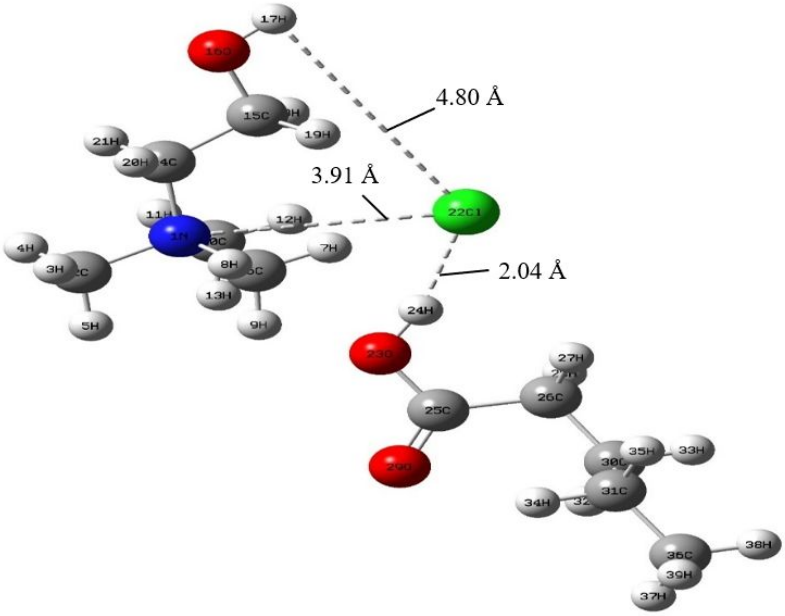


Fig. S3. Optimized equilibrium geometry structure of [Ch]Cl:VA (1:1) DES. Atoms are colored according to type: C (gray), O (red), N (blue), H (white), and Cl (light green). Bond angle between C14-C15-O16 (102.69 º), C15-O16-H17 (107.40 º), C2-N1-C14 (107.96 º), and N1-C14-C15 (116.53 º).

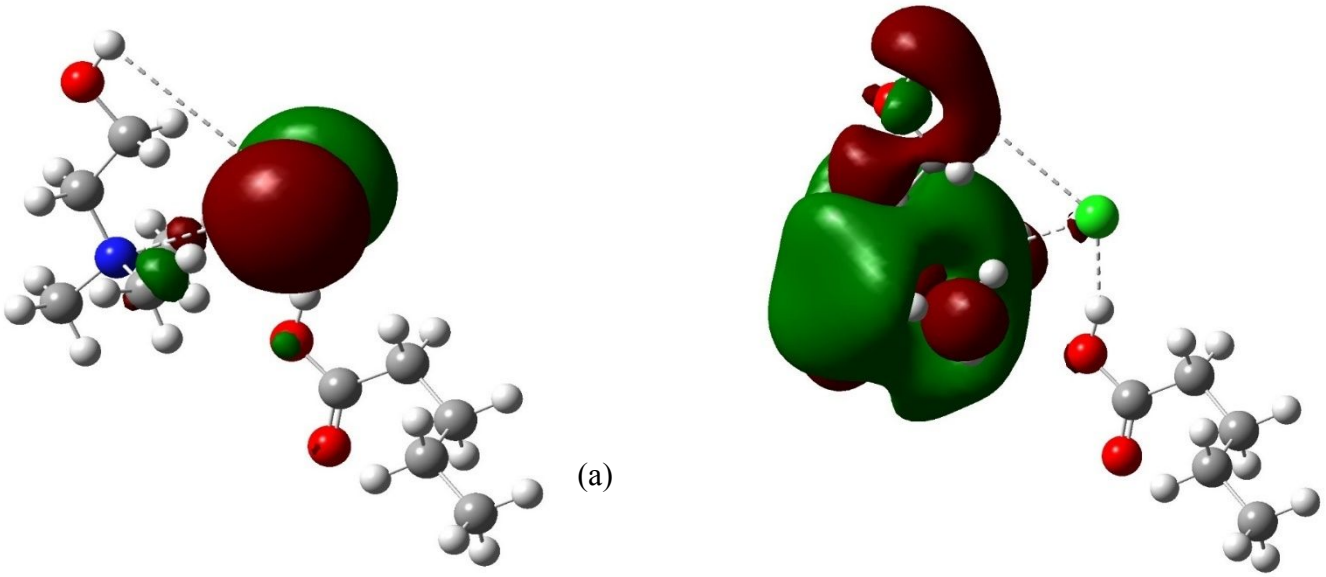


Fig. S4. Frontier molecular orbitals of [Ch]Cl:VA DES: (a) HOMO and (b) LUMO

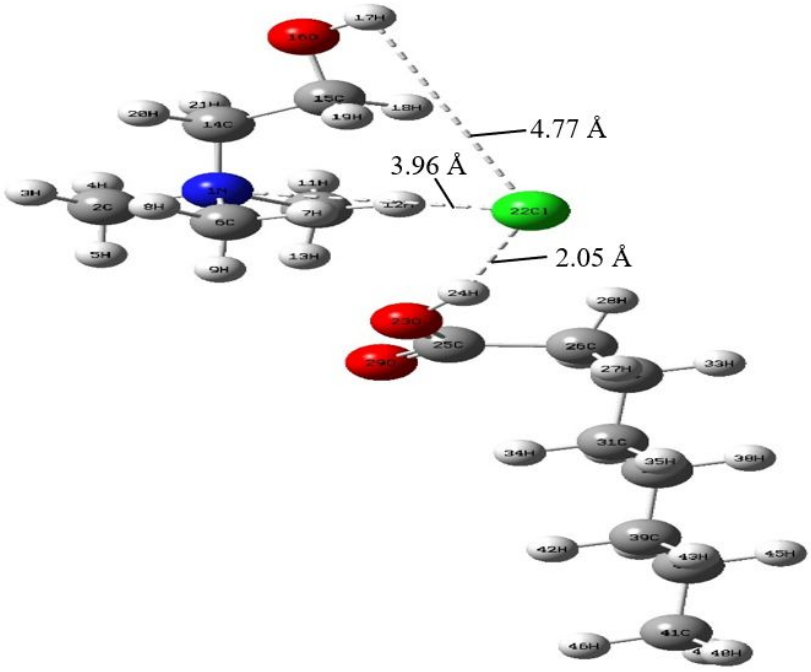


Fig. S5. Optimized equilibrium geometry structure of [Ch]Cl:CA (1:1) DES. Atoms are colored according to type: C (gray), O (red), N (blue), H (white), and Cl (light green). Bond angle between C14-C15-O16 (102.77 º), C15-O16-H17 (107.33 º), C2-N1-C14 (108.00 º), and N1-C14-C15 (116.44 º).

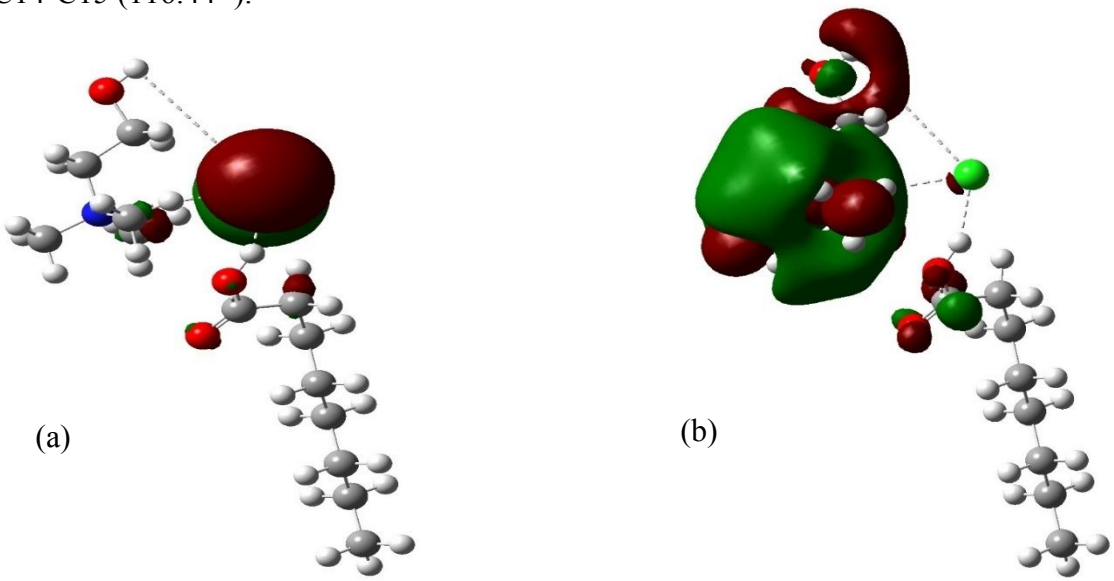


Fig. S6. Frontier molecular orbitals of [Ch]Cl:CA DES: (a) HOMO and (b) LUMO

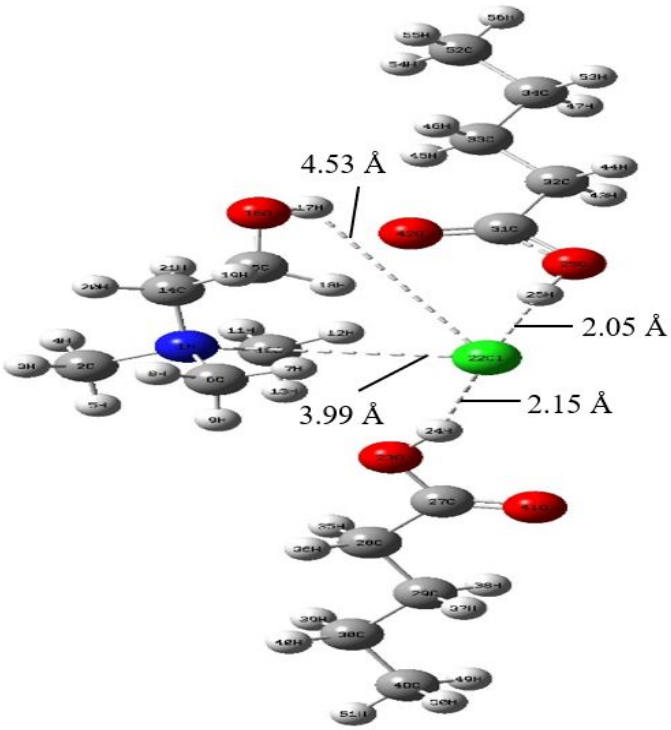
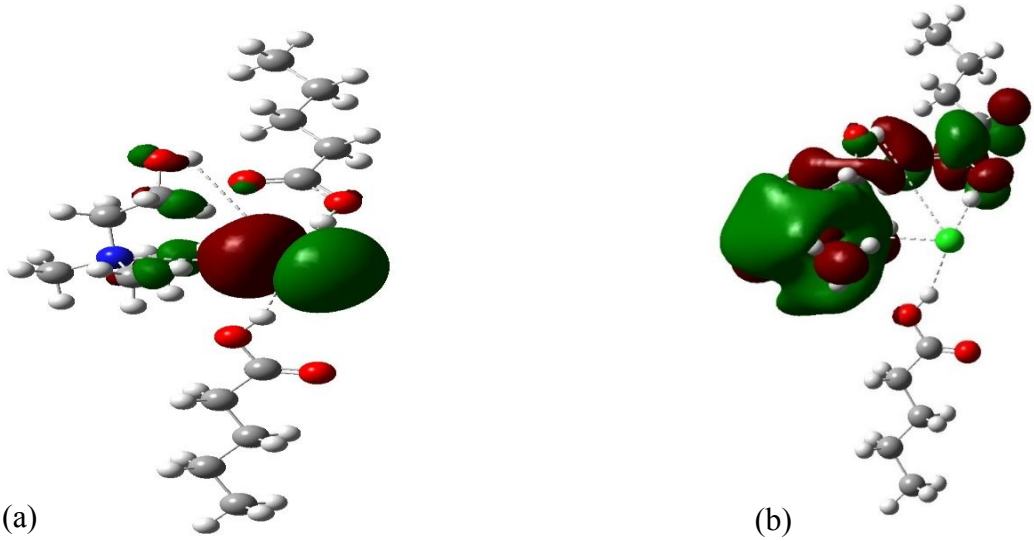


Fig. S7. Optimized equilibrium geometry structure of [Ch]Cl:VA (1:2) DES. Atoms are colored according to type: C (gray), O (red), N (blue), H (white), and Cl (light green). Bond angle between C14-C15-O16 (107.99 º), C15-O16-H17 (105.01 º), C2-N1-C14 (108.72 º), and N1-C14-C15 (116.09 º).



(a) (b)

Fig. S8. Frontier molecular orbitals of [Ch]Cl:VA (1:2) DES: (a) HOMO and (b) LUMO

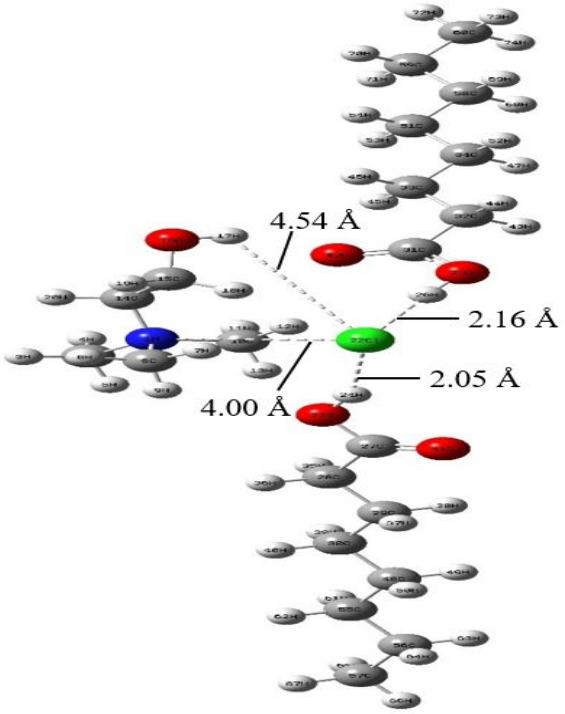


Fig. S9. Optimized equilibrium geometry structure of [Ch]Cl:CA (1:2) DES. Atoms are colored according to type: C (gray), O (red), N (blue), H (white), and Cl (light green). Bond angle between C14-C15-O16 (108.05 º), C15-O16-H17 (105.02 º), C2-N1-C14 (108.76 º), and N1-C14-C15 (116.09 º).

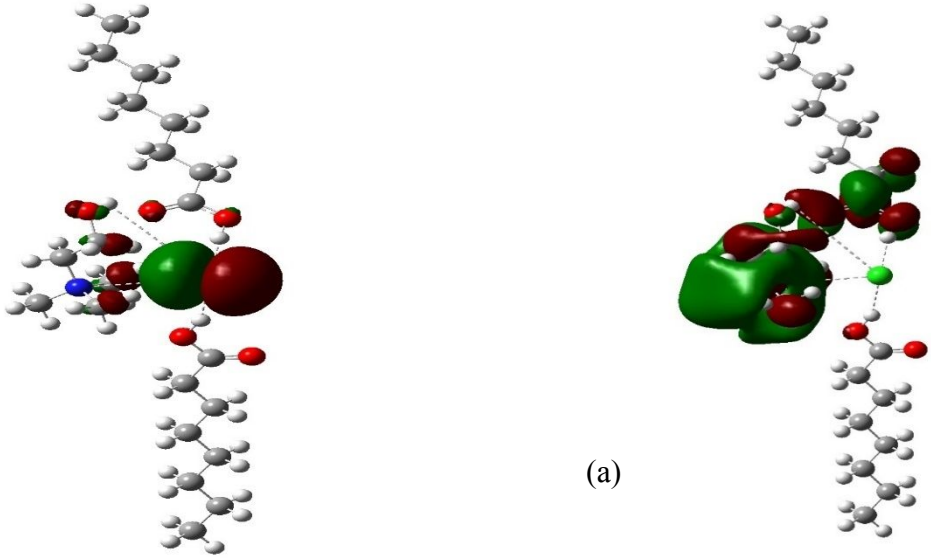


Fig. S10. Frontier molecular orbitals of [Ch]Cl:CA DES (1:2) (a) HOMO and (b) LUMO

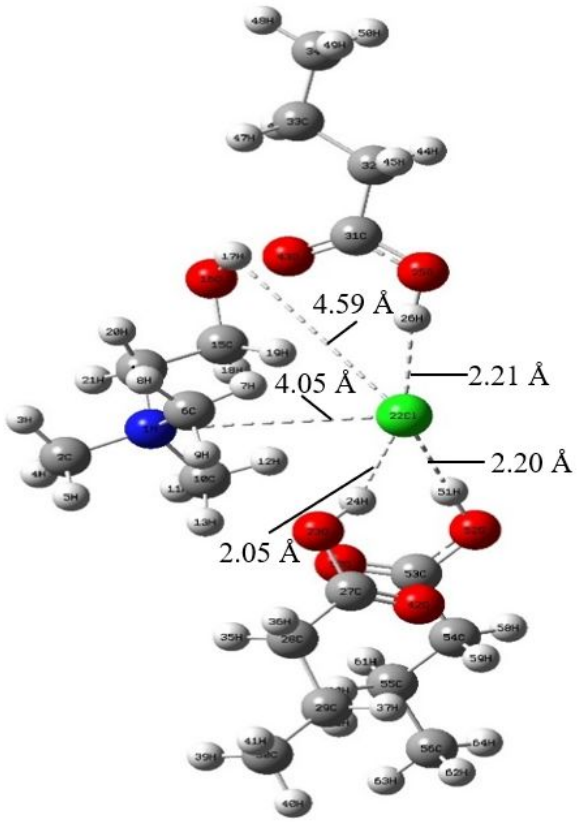


Fig. S11. Optimized equilibrium geometry structure of [Ch]Cl:BA (1:3) DES. Atoms are colored according to type: C (gray), O (red), N (blue), H (white), and Cl (light green). Bond angle between C14-C15-O16 (107.96 º), C15-O16-H17 (105.16 º), C2-N1-C14 (108.79 º), and N1-C14-C15 (116.01 º).

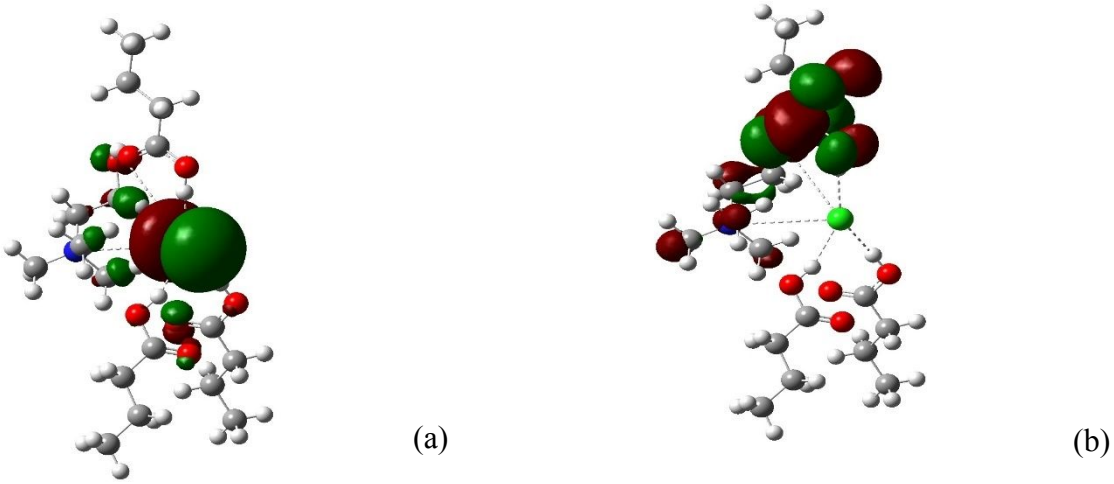


Fig. S12. Frontier molecular orbitals of [Ch]Cl:BA (1:3) DES: (a) HOMO and (b) LUMO

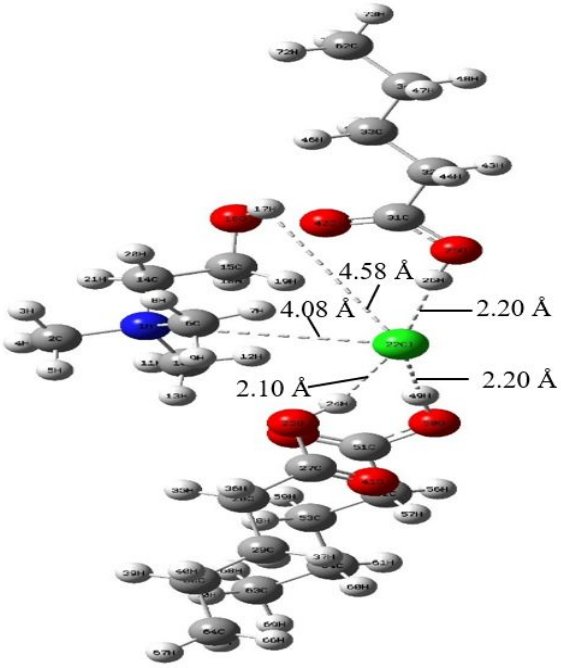
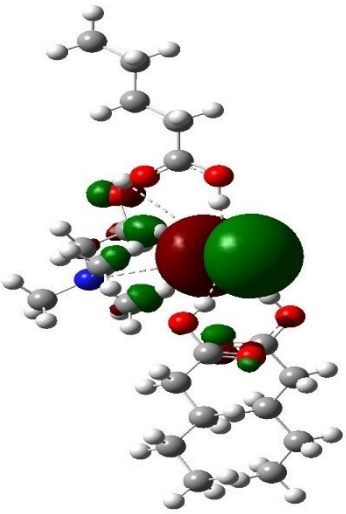


Fig. S13. Optimized equilibrium geometry structure of [Ch]Cl:BA (1:3) DES. Atoms are colored according to type: C (gray), O (red), N (blue), H (white), and Cl (light green). Bond angle between C14-C15-O16 (108.04 º), C15-O16-H17 (105.19 º), C2-N1-C14 (108.83 º), and N1-C14-C15 (115.97 º).

(a)



(b)

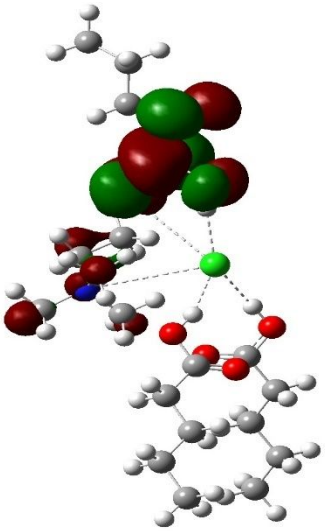


Fig. S14. Frontier molecular orbitals of [Ch]Cl:VA (1:3) DES: (a) HOMO and (b) LUMO

Table S1. Viscosity of DESs synthesized in this study

DES	Mole ratio	Viscosity (cP)
[Ch]Cl:BA	1:2	1757 ± 14
	1:3	54.1±3.5
[Ch]Cl:VA	1:2	1497 ± 41
	1:3	44.5 ± 11
[Ch]Cl:CA	1:2	1594.7 ± 31
	1:3	1561.3 ± 70

Table S2. Molecular parameters of choline chloride and carboxylic acids. The global hardness, $\eta = I-A/2$; and chemical softness, $S = 1/2\eta$; where I = ionization energy and A = electron affinity.

HBA and HBDs	Є HOMO (eV)	Є LUMO (eV)	ΔЄ (eV)	I	A	μ	χ	η	S	Dipole moment (Debye)
[Ch]Cl	-0.17186	0.01291	0.18477	0.17186	-0.01291	-0.07948	0.079475	0.092385	5.412134	11.5653
BA	-0.27479	0.01038	0.28517	0.27479	-0.01038	-0.13221	0.132205	0.142585	3.50668	1.3672
2BA	-0.28011	0.00365	0.28376	0.28011	-0.00365	-0.13823	0.13823	0.14188	3.524105	0.0002
3BA	-0.26809	0.00071	0.2688	0.26809	-0.00071	-0.13369	0.13369	0.1344	3.720238	2.294
VA	-0.27462	0.01054	0.28516	0.27462	-0.01054	-0.13204	0.13204	0.14258	3.506803	1.3438
2VA	-0.27952	0.004	0.28352	0.27952	-0.004	-0.13776	0.13776	0.14176	3.527088	0.0245
3VA	-0.26775	0.00125	0.269	0.26775	-0.00125	-0.13325	0.13325	0.1345	3.717472	2.3368
CA	-0.27448	0.01079	0.28527	0.27448	-0.01079	-0.13185	0.131845	0.142635	3.505451	1.3059
2CA	-0.27861	0.00435	0.28296	0.27861	-0.00435	-0.13713	0.13713	0.14148	3.534068	0.0606

Table S3. Molecular indices of DESs calculated from DFT data.

DES	Molar ratio	S	η	μ = (ЄHOMO +Є LUMO)/2	χ =(I+A)/2
[Ch]Cl:BA	1:1	4.577078	0.10924	-0.10005	0.10005
	1:2	4.321895	0.11569	-0.10416	0.10416
	1:3	4.039098	0.12379	-0.11343	0.11343
[Ch]Cl:VA	1:1	4.577497	0.10923	-0.10014	0.10014
	1:2	4.254595	0.11752	-0.10473	0.10473
	1:3	4.03812	0.12382	-0.11338	0.11338
[Ch]Cl:CA	1:1	4.548763	0.10992	-0.09863	0.09863
	1:2	4.264392	0.11725	-0.10437	0.10437

[a]Standard uncertainties, u, of S, η, μ, and χ are u(S) = 0.016, u(η) = 0.00099, u(μ) = 0.0069, and u(χ) = 0.0067.

Table S4. Literature data of ionic liquids and organic solvents used for ternary plot

Solvent	E_T^N	α	β	π*
bmim][SbF_6] [1]	0.673	0.639	0.146	1.039
[bmim][BF_4 [1]	0.67	0.627	0.376	1.047
[bmim][PF_6 [1]	0.669	0.634	0.207	1.032
[bmim][TfO] [1]	0.656	0.625	0.464	1.006
[bmim][$N(Tf)_2$] [1]	0.644	0.617	0.243	0.984
[bm2im][BF_4] [1]	0.576	0.402	0.363	1.083
[bmpy][$N(Tf)_2$] [1]	0.544	0.427	0.252	0.954
[bm2im][$N(Tf)_2$ [1]	0.541	0.381	0.239	1.01
[EMIm][PF_6] [1]	0.676	0.66	0.2	0.99
[EMIm][NTf_2] [2]	0.657	0.76	0.28	0.9
[EMIm][ClO_4] [2]	0.67	0.56	0.41	1.11
[EMIm][DCA] [2]	0.648	0.53	0.35	1.08
[EMIm][NO_3] [2]	0.642	0.48	0.66	1.13
[EMIm][AC] [2]	0.59	0.4	0.95	1.09
[HOEMIm][PF_6] [2]	0.957	1.17	0.15	1.11
[HOEMIm][NTf_2] [2]	0.929	1.17	0.34	1.03
[HOEMIm][ClO_4] [2]	0.914	1.06	0.16	1.13
[HOEMIm][DCA] [2]	0.784	0.8	0.51	1.11
[HOEMIm][NO_3] [2]	0.769	0.77	0.65	1.11
[HOEMIm][Cl] [2]	0.769	0.73	0.68	1.16
[HOEMIm][AC] [2]	0.633	0.53	0.9	1.04

Table S4. *Continued*:

Solvent	E_T^N	α	β	π*
[3-MBP][BF_4] [3]	0.651	0.56	0.423	1.071
[4-MP][BF_4] [3]	0.636	0.53	0.533	1.066
Acetonitrile [1]	0.46	0.35	0.37	0.799
Acetone [1]	0.35	0.202	0.539	0.704
Dichloromethane [3]	0.309	0.04	0.578	0.733
Toluene [1]	0.1	-0.213	0.077	0.532
Methanol [3]	0.762	1.03	0.578	0.771
1,1,2,2-Tetrachloroethane [4]	0.309	0	0	0.95
Nitrobenzene [4]	0.324	0	0.3	1.01
1,1,1-Trichloroethane [4]	0.17	0	0	0.49
Benzene [4]	0.111	0	0.1	0.59
Acetophenone [4]	0.306	0.04	0.49	0.9
Toluene [4]	0.0099	0	0.11	0.54
1,4-dioxane [4]	0.164	0	0.37	0.55
Cyclohexanone [4]	0.281	0	0.53	0.76
DMSO [4]	0.444	0	0.76	1
Ethyl acetate [4]	0.228	0	0.45	0.55
Tetrahydrofuran [4]	0.207	0	0.55	0.58
Ethanol [5]	-	0.98	0.83	0.51

References

(1) Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, J. M.; Salter, P. A.; Welton, T., Solvent–solute interactions in ionic liquids. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2790 –2794.

(2) Zhang, S.; Qi, X.; Ma, X.; Lu, L.; Deng, Y., Hydroxyl ionic liquids: the differentiating effect of hydroxyl on polarity due to ionic hydrogen bonds between hydroxyl and anions. *J. Phys. Chem. B* **2010**, *114*, 3912–3920.

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(4) Chiappe, C.; Pieraccini, D., Determination of Ionic Liquids Solvent Properties Using an Unusual Probe: The Electron Donor−Acceptor Complex between 4, 4 ‘-bis (Dimethylamino)-benzophenone and Tetracyanoethene. *J. Phys. Chem. A* **2006**, *110*, 4937–4941.

(5) Buhvestov, U.; Rived, F.; Ràfols, C.; Bosch, E.; Rosés, M., Solute–solvent and solvent–solvent interactions in binary solvent mixtures. Part 7. Comparison of the enhancement of the water structure in alcohol–water mixtures measured by solvatochromic indicators. *J. Phys. Org. Chem.* **1998**, *11*, 185–192.