Electronic Supplementary Information to: On the composition and isomerism effect in the thermal and structural properties of choline chloride/hydroxyphenol deep eutectic solvents

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Table S1: Number of molecules and box dimensions of the simulated molecular dynamics (MD) systems formed by choline chloride (ChCl) with the catechol (Cate), resorcinol (Reso), and hydroquinone (Hydro) hydrogen-bond donors (HBDs) at different molar ratios of the components.

		ChCl	HBD	Box edge (Å)
ChCl/Cate	1:0.75	388	291	49.97
	1:1	349	349	49.99
	1:2	246	492	49.97
	1:3	191	573	49.97
ChCl/Reso	1:0.75	392	294	50.17
	1:1	348	348	50.02
	1:2	246	492	50.01
	1:3	190	570	49.99
ChCl/Hydro	1:0.75	388	291	50.07
	1:1	346	346	49.99
	1:2	243	486	49.98
	1:3	189	567	50.05

Table S2: Liquid-glass transition temperature (T_g), cold crystallization temperature (T_{cc}), and melting temperature (T_m) obtained from density scanning calorimetry thermograms for the ChCl/Cate, ChCl/Reso, and ChCl/Hydro mixtures at different molar ratios of the components, together with the difference (ΔT) between the T_m experimental values and those calculated from the ideal phase diagrams for the solid-liquid equilibrium (SLE) between the components ($T_{m,\,ideal}$). Values in Kelvin degrees.

Mixture		T_g	T_{cc}	T_m	$T_{m,\,ideal}$	ΔT
ChCl/Cate	1:0.75	-	264	-	370	-
	1:1	193	256	318		-52
	1:2	-	-	328		-42
	1:3	211	253	318		-52
ChCl/Reso	1:0.75	195	250	290	374	-84
	1:1	-	-	302		-72
	1:2	192	-	-		-
	1:3	213	-	-		-
ChCl/Hydro	1:0.75	-	-	326	429	-103
	1:1	-	-	315		-114
	1:2	-	-	316		-113

Table S3: Enthalpy of fusion ($\Delta_{cr}H_m$) and T_m of the pristine compounds taken from literature data and employed in this work to build the ideal SLE phase diagrams.

Compound	$\Delta_{cr}H_m$(kJ mol^{-1})	T_m(K)	ref.
ChCl	13.8	∼687	[1]
Cate	22.5	377.5	[2]
Reso	19.4	382.5	[2]
Hydro	26.9	445.4	[2]

Table S4: Number of H-bonds and average number of H-bonds *per* chloride anion for the Cl-HO_{HBD} and Cl-HO_{Ch} interactions calculated from the MD simulations of the ChCl/Cate, ChCl/Reso, and ChCl/Hydro mixtures at different molar ratios of the components. Atom nomenclature according to Figure 1 of the manuscript.

		Cl-HO_{HBD}		Cl-HO_{ch}	
		n° H-bond	n° H-bond / n° Cl^-	n° H-bond	n° H-bond / n° Cl^-
ChCl/Cate	1:0.75	543.76	1.40	372.01	0.96
	1:1	641.54	1.84	322.67	0.92
	1:2	798.26	3.24	173.47	0.56
	1:3	760.05	3.98	77.18	0.40
ChCl/Reso	1:0.75	576.78	1.47	378.92	0.97
	1:1	675.48	1.94	328.07	0.94
	1:2	850.49	3.46	187.26	0.76
	1:3	783.57	4.12	103.90	0.55
ChCl/Hydro	1:0.75	567.91	1.46	380.03	0.98
	1:1	666.92	1.93	332.86	0.96
	1:2	829.75	3.41	200.62	0.83
	1:3	801.60	4.24	116.22	0.61

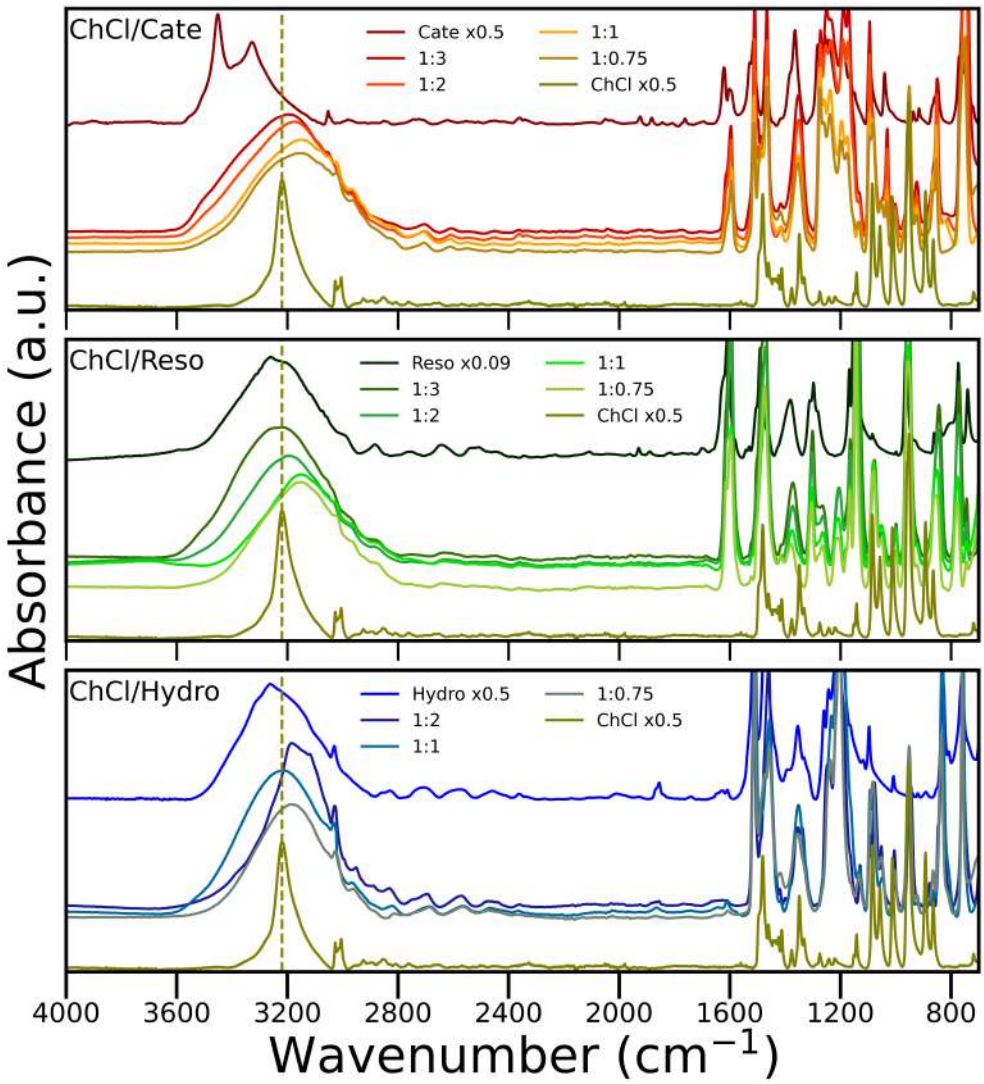

Figure S1: Attenuated total reflection Fourier transform infrared spectra collected on the ChCl/Cate, ChCl/Reso, and ChCl/Hydro mixtures at different molar ratios of the components. A vertical dashed line corresponding to the maximum of the O-H stretching absorption for the ChCl compound is reported as a guide to the eye.

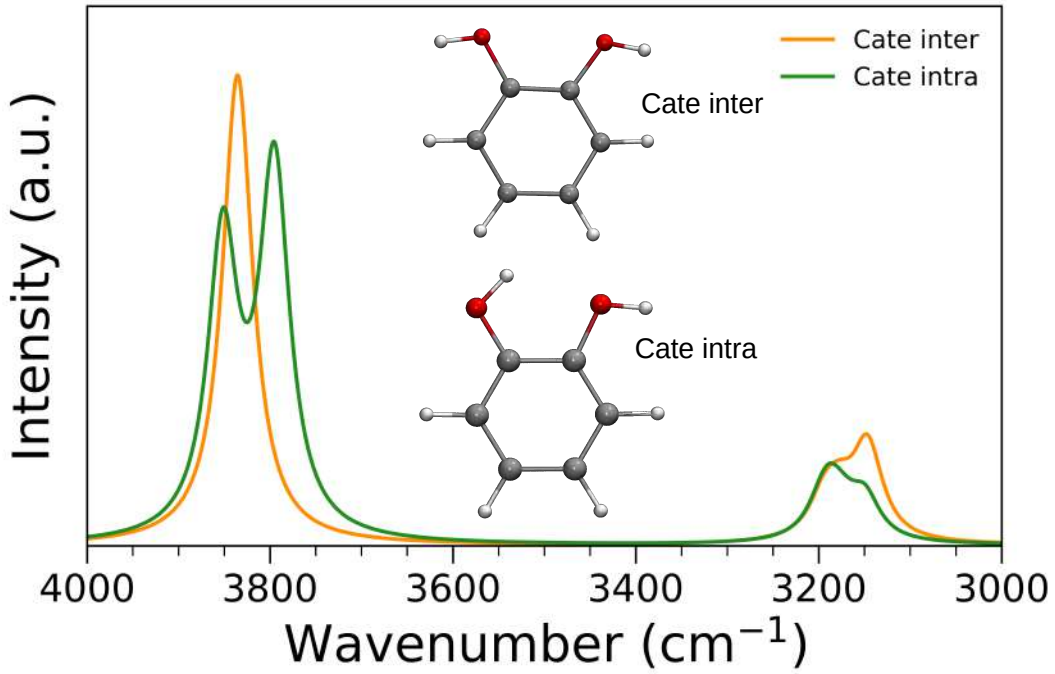

Figure S2: Simulated infrared spectra after geometrical optimization in gas-phase conditions for the two rotamers of the Cate molecule, Cate inter and Cate intra, at the density functional theory B3LYP/6-311++G(d,p)/GD3 level of theory.

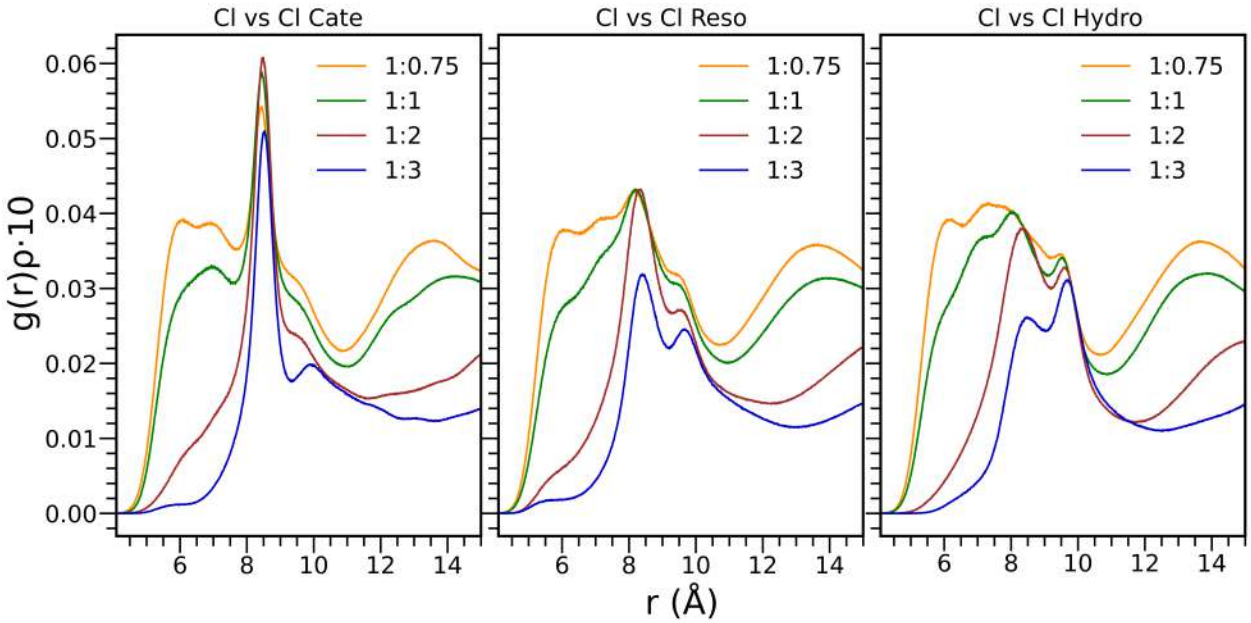

Figure S3: Radial distribution functions multiplied by the number density of the observed species, $g(r)\rho$'s, for the Cl-Cl pairs calculated from the MD simulations of the ChCl/Cate (left), ChCl/Reso (middle), and ChCl/Hydro (right) mixtures at different molar ratios of the components.

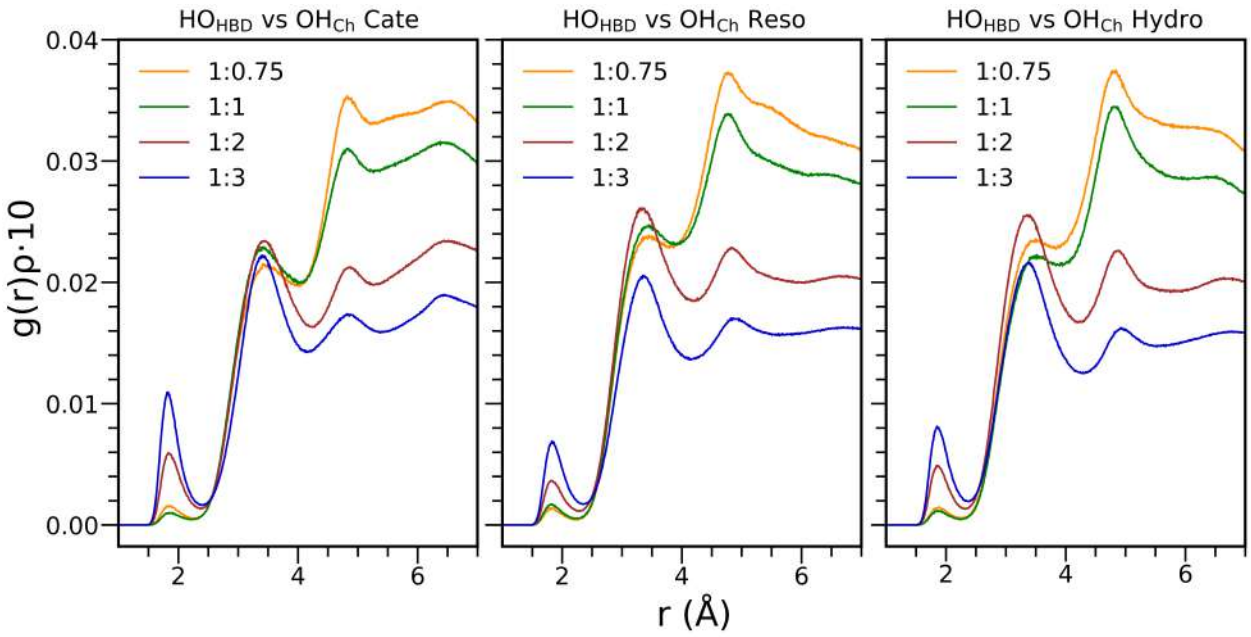

Figure S4: Radial distribution functions multiplied by the number density of the observed species, $g(r)\rho$'s, for the HO_{HBD}-OH_{Ch} pairs calculated from the MD simulations of the ChCl/Cate (left), ChCl/Reso (middle), and ChCl/Hydro (right) mixtures at different molar ratios of the components. Atom nomenclature according to Figure 1 of the manuscript.

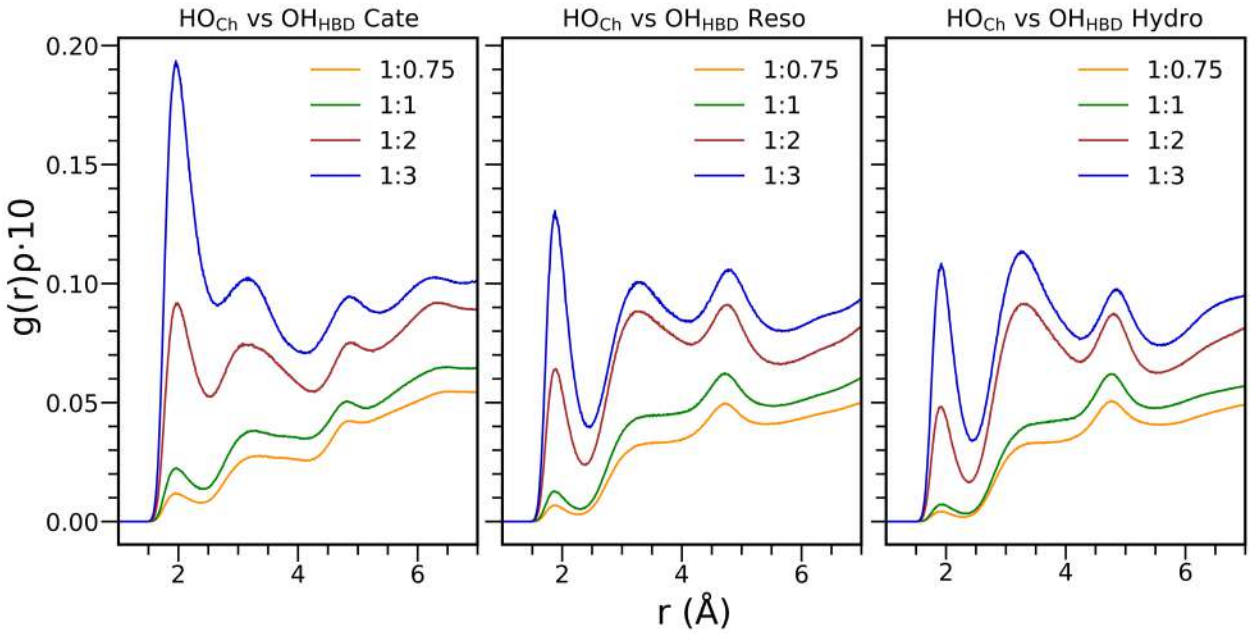

Figure S5: Radial distribution functions multiplied by the number density of the observed species, $g(r)\rho$'s, for the HO_{Ch}-OH_{HBD} pairs calculated from the MD simulations of the ChCl/Cate (left), ChCl/Reso (middle), and ChCl/Hydro (right) mixtures at different molar ratios of the components. Atom nomenclature according to Figure 1 of the manuscript.

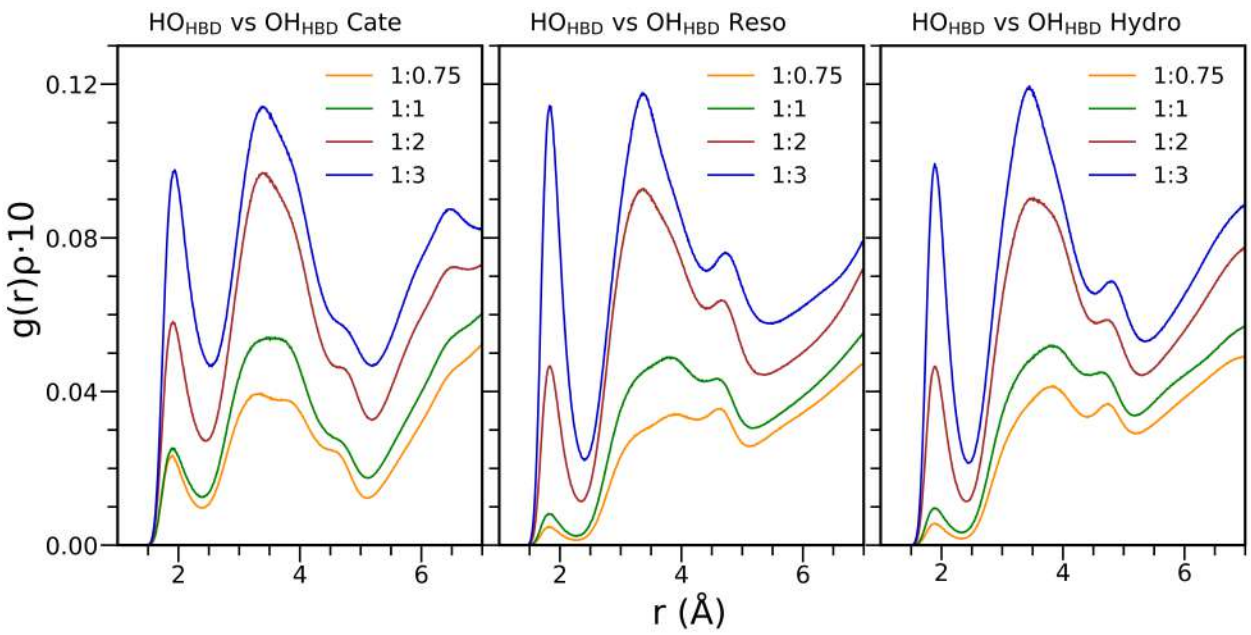

Figure S6: Radial distribution functions multiplied by the number density of the observed species, $g(r)\rho$'s, for the HO_{HBD}-OH_{HBD} pairs calculated from the MD simulations of the ChCl/Cate (left), ChCl/Reso (middle), and ChCl/Hydro (right) mixtures at different molar ratios of the components. Atom nomenclature according to Figure 1 of the manuscript.

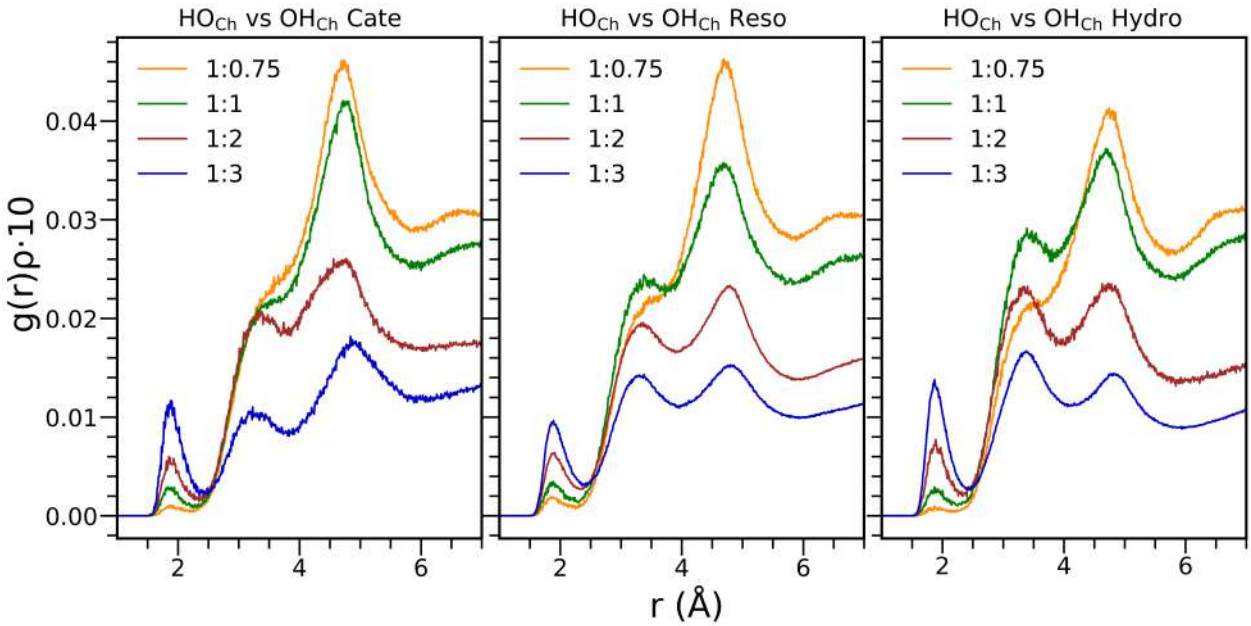

Figure S7: Radial distribution functions multiplied by the number density of the observed species, $g(r)\rho$'s, for the HO_{Ch}-OH_{Ch} pairs calculated from the MD simulations of the ChCl/Cate (left), ChCl/Reso (middle), and ChCl/Hydro (right) mixtures at different molar ratios of the components. Atom nomenclature according to Figure 1 of the manuscript.

References

[1] Adriaan van den Bruinhorst et al. “Defying decomposition: the curious case of choline chloride”. In: *Nat. Commun.* 14.1 (2023), p. 6684.

[2] Sergey P Verevkin and Svetlana A Kozlova. “Di-hydroxybenzenes: Catechol, resorcinol, and hydroquinone: Enthalpies of phase transitions revisited”. In: *Thermochim. Acta* 471.1-2 (2008), pp. 33–42.