Electronic Supporting Information for:

Insights into the effect of lithium doping on the deep eutectic solvent choline chloride: urea

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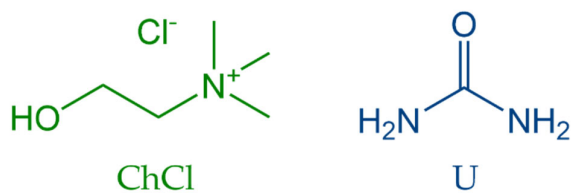
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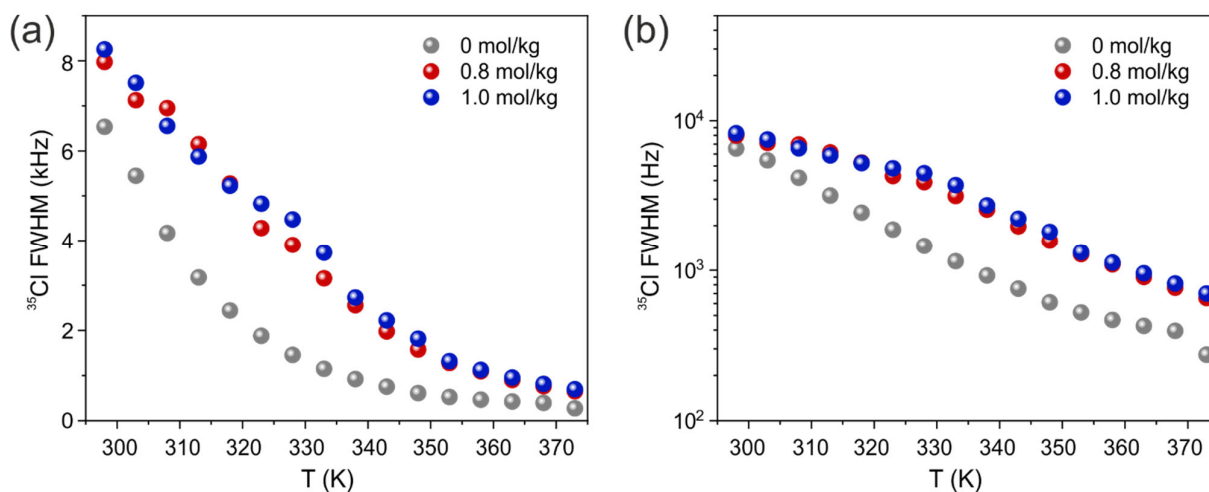
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<p align="center">**Table S1**. The main types of DESs [1,2].</p>

Type	General composition	Example
I	Metal salt + organic salt	$ZnCl_2$ + ChCl
II	Metal salt hydrate + organic salt	$CoCl_2 \cdot 6\ H_2O$ + ChCl
III	Organic salt + Hydrogen Bond Donor	ChCl + U
IV	Metal salt (hydrate) + Hydrogen Bond Donor	$ZnCl_2$ + U
V	Molecular non-ionic Hydrogen Bond Donor and Acceptor	thymol + menthol

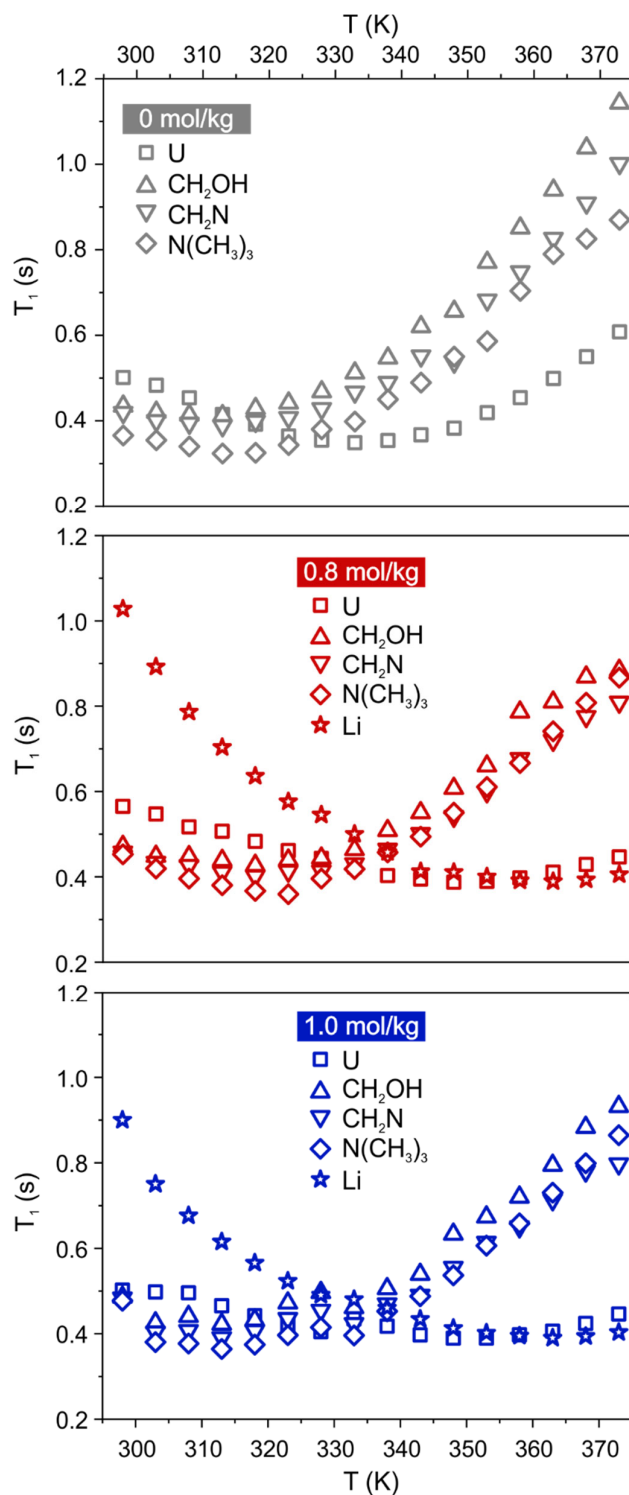**Figure S1.** Chemical structure of choline chloride (ChCl) and urea (U).

Figure S2. ^{35}Cl NMR (a) linear and (b) log-scaled full width at half maximum (FWHM) of ChCl:U-LiCl(0) (grey), ChCl:U-LiCl(0.8) (red), and ChCl:U-LiCl(1.0) (blue), as a function of temperature.

Table S2. Temperature-dependent ^1H and ^7Li self-diffusion coefficients *D* (in m^2s^{-1}) measured for ChCl:U−LiCl(0), ChCl:U−LiCl(0.8) and ChCl:U−LiCl(1.0). Maximum errors are estimated to be 3% for ^1H and 5% for ^7Li.

T (K)	ChCl:U−LiCl(0)		ChCl:U−LiCl(0.8)			ChCl:U−LiCl(1.0)		
	U	Ch	U	Ch	Li	U	Ch	Li
298	$3.03 \cdot 10^{-12}$	$2.44 \cdot 10^{-12}$	$1.20 \cdot 10^{-12}$	$1.08 \cdot 10^{-12}$		$1.02 \cdot 10^{-12}$	$8.20 \cdot 10^{-13}$	
303	$5.00 \cdot 10^{-12}$	$3.72 \cdot 10^{-12}$	$1.80 \cdot 10^{-12}$	$1.55 \cdot 10^{-12}$		$1.70 \cdot 10^{-12}$	$1.10 \cdot 10^{-12}$	
308	$7.04 \cdot 10^{-12}$	$4.74 \cdot 10^{-12}$	$2.69 \cdot 10^{-12}$	$2.17 \cdot 10^{-12}$		$2.20 \cdot 10^{-12}$	$1.50 \cdot 10^{-12}$	
313	$1.01 \cdot 10^{-11}$	$6.24 \cdot 10^{-12}$	$3.97 \cdot 10^{-12}$	$2.97 \cdot 10^{-12}$		$2.80 \cdot 10^{-12}$	$2.00 \cdot 10^{-12}$	
318	$1.44 \cdot 10^{-11}$	$8.27 \cdot 10^{-12}$	$5.72 \cdot 10^{-12}$	$3.96 \cdot 10^{-12}$	$2.44 \cdot 10^{-12}$	$4.30 \cdot 10^{-12}$	$2.90 \cdot 10^{-12}$	$1.84 \cdot 10^{-12}$
323	$1.98 \cdot 10^{-11}$	$1.10 \cdot 10^{-11}$	$8.21 \cdot 10^{-12}$	$5.29 \cdot 10^{-12}$	$3.42 \cdot 10^{-12}$	$6.00 \cdot 10^{-12}$	$4.10 \cdot 10^{-12}$	$2.76 \cdot 10^{-12}$
328	$2.66 \cdot 10^{-11}$	$1.45 \cdot 10^{-11}$	$1.13 \cdot 10^{-11}$	$6.85 \cdot 10^{-12}$	$3.93 \cdot 10^{-12}$	$7.37 \cdot 10^{-12}$	$5.10 \cdot 10^{-12}$	$3.27 \cdot 10^{-12}$
333	$3.46 \cdot 10^{-11}$	$1.87 \cdot 10^{-11}$	$1.32 \cdot 10^{-11}$	$8.11 \cdot 10^{-12}$	$5.40 \cdot 10^{-12}$	$1.07 \cdot 10^{-11}$	$6.98 \cdot 10^{-12}$	$4.66 \cdot 10^{-12}$
338	$4.42 \cdot 10^{-11}$	$2.39 \cdot 10^{-11}$	$1.90 \cdot 10^{-11}$	$1.12 \cdot 10^{-11}$	$7.70 \cdot 10^{-12}$	$1.54 \cdot 10^{-11}$	$9.39 \cdot 10^{-12}$	$6.87 \cdot 10^{-12}$
343	$5.47 \cdot 10^{-11}$	$2.98 \cdot 10^{-11}$	$2.51 \cdot 10^{-11}$	$1.44 \cdot 10^{-11}$	$1.01 \cdot 10^{-11}$	$2.01 \cdot 10^{-11}$	$1.20 \cdot 10^{-11}$	$8.82 \cdot 10^{-12}$
348	$7.24 \cdot 10^{-11}$	$3.83 \cdot 10^{-11}$	$3.20 \cdot 10^{-11}$	$1.83 \cdot 10^{-11}$	$1.29 \cdot 10^{-11}$	$2.63 \cdot 10^{-11}$	$1.56 \cdot 10^{-11}$	$1.17 \cdot 10^{-11}$
353	$8.52 \cdot 10^{-11}$	$4.63 \cdot 10^{-11}$	$4.10 \cdot 10^{-11}$	$2.37 \cdot 10^{-11}$	$1.70 \cdot 10^{-11}$	$3.80 \cdot 10^{-11}$	$2.23 \cdot 10^{-11}$	$1.71 \cdot 10^{-11}$
358	$9.87 \cdot 10^{-11}$	$5.45 \cdot 10^{-11}$	$5.04 \cdot 10^{-11}$	$2.91 \cdot 10^{-11}$	$2.12 \cdot 10^{-11}$	$4.79 \cdot 10^{-11}$	$2.76 \cdot 10^{-11}$	$2.04 \cdot 10^{-11}$
363	$1.18 \cdot 10^{-10}$	$6.49 \cdot 10^{-11}$	$6.24 \cdot 10^{-11}$	$3.63 \cdot 10^{-11}$	$2.77 \cdot 10^{-11}$	$5.80 \cdot 10^{-11}$	$3.37 \cdot 10^{-11}$	$2.51 \cdot 10^{-11}$
368	$1.36 \cdot 10^{-10}$	$7.54 \cdot 10^{-11}$	$7.72 \cdot 10^{-11}$	$4.70 \cdot 10^{-11}$	$3.97 \cdot 10^{-11}$	$6.98 \cdot 10^{-11}$	$4.06 \cdot 10^{-11}$	$3.03 \cdot 10^{-11}$
373	$1.58 \cdot 10^{-10}$	$8.92 \cdot 10^{-11}$	$9.26 \cdot 10^{-11}$	$5.60 \cdot 10^{-11}$	$4.43 \cdot 10^{-11}$	$8.37 \cdot 10^{-11}$	$4.83 \cdot 10^{-11}$	$3.65 \cdot 10^{-11}$

Table S3. Parameters obtained from the linear fit of the Arrhenius plot of the diffusion data in the whole temperature range (298-373 K for ^{1}H, 318-373 K for ^{7}Li).

Sample	Species	lnA (m^2s^{-1})	E_a^{transl} $(kJmol^{-1})$	R^2
ChCl:U−LiCl(0)	U	-6.8445	48.1	0.990
	Ch	-8.732	44.3	0.998
ChCl:U−LiCl(0.8)	U	-5.7644	53.4	0.996
	Ch	-8.0666	48.1	0.999
	Li	-6.6553	53.2	0.997
ChCl:U−LiCl(1.0)	U	-5.3153	55.1	0.998
	Ch	-6.9686	51.8	0.999
	Li	-6.2722	54.7	0.995

Figure S3. ^{1}H and ^{7}Li T_1 relaxation times of ChCl:U-LiCl(0) (top, grey), ChCl:U-LiCl(0.8) (middle, red), and ChCl:U-LiCl(1.0) (bottom, blue), as a function of temperature. Maximum errors are estimated to be 3%.

Table S4. Best-fit parameters obtained for all proton and lithium nuclei using the BPP model. Maximum errors are estimated to be 15% for τ_0, 5% for E_a^{rot}, 2% for C.

Site	ChCl:U−LiCl(0)			ChCl:U−LiCl(0.8)			ChCl:U−LiCl(1.0)		
	C [10^9] (s^{-2})	E_a^{rot} (kJmol^{-1})	τ_0 (s)	C [10^9] (s^{-2})	E_a^{rot} (kJmol^{-1})	τ_0 (s)	C [10^9] (s^{-2})	E_a^{rot} (kJmol^{-1})	τ_0 (s)
U[a]	6.3	30.6	$3.0 \cdot 10^{-15}$	5.6	28.4	$3.0 \cdot 10^{-14}$	-	-	-
U[b]	6.3	31.1	$2.5 \cdot 10^{-15}$	5.7	28.9	$9.9 \cdot 10^{-15}$	5.7	27.2	$1.7 \cdot 10^{-14}$
CH_2OH	5.4	26.8	$5.9 \cdot 10^{-15}$	5.2	25.6	$1.1 \cdot 10^{-14}$	5.1	24.1	$1.9 \cdot 10^{-14}$
CH_2N	5.7	26.4	$7.5 \cdot 10^{-15}$	5.5	25.5	$1.2 \cdot 10^{-14}$	5.4	24.2	$1.9 \cdot 10^{-14}$
$N(CH_3)_3$	6.7	28.7	$3.1 \cdot 10^{-15}$	5.9	29.0	$3.3 \cdot 10^{-15}$	5.9	27.7	$5.2 \cdot 10^{-15}$
Li	-	-	-	2.2	24.2	$1.7 \cdot 10^{-13}$	2.2	20.0	$6.9 \cdot 10^{-13}$

[a] T_1 curves fitted in the range 308-373 K and 323-373 K for samples ChCl:U-LiCl(0) and ChCl:U-LiCl(0.8), respectively.
[b] T_1 curves fitted in the range 333-373K for all samples.

Table S5. ^{1}H rotational correlation times τ_c (s) calculated for ChCl:U-LiCl(0) using the BPP model.

T (K)	U*	CH$_2$OH	CH$_2$N	N(CH$_3$)$_3$
298	-	2.94·10^{-10}	3.14·10^{-10}	3.33·10^{-10}
303	-	2.46·10^{-10}	2.64·10^{-10}	2.75·10^{-10}
308	4.66·10^{-10}	2.07·10^{-10}	2.23·10^{-10}	2.29·10^{-10}
313	3.85·10^{-10}	1.75·10^{-10}	1.89·10^{-10}	1.91·10^{-10}
318	3.20·10^{-10}	1.49·10^{-10}	1.61·10^{-10}	1.61·10^{-10}
323	2.67·10^{-10}	1.27·10^{-10}	1.38·10^{-10}	1.36·10^{-10}
328	2.25·10^{-10}	1.09·10^{-10}	1.19·10^{-10}	1.15·10^{-10}
333	1.90·10^{-10}	9.42·10^{-11}	1.03·10^{-10}	9.84·10^{-11}
338	1.61·10^{-10}	8.17·10^{-11}	8.92·10^{-11}	8.44·10^{-11}
343	1.38·10^{-10}	7.11·10^{-11}	7.78·10^{-11}	7.27·10^{-11}
348	1.18·10^{-10}	6.21·10^{-11}	6.81·10^{-11}	6.29·10^{-11}
353	1.02·10^{-10}	5.45·10^{-11}	5.99·10^{-11}	5.46·10^{-11}
358	8.78·10^{-11}	4.79·10^{-11}	5.28·10^{-11}	4.77·10^{-11}
363	7.62·10^{-11}	4.23·10^{-11}	4.68·10^{-11}	4.17·10^{-11}
368	6.64·10^{-11}	3.75·10^{-11}	4.15·10^{-11}	3.67·10^{-11}
373	5.81·10^{-11}	3.34·10^{-11}	3.70·10^{-11}	3.23·10^{-11}

* T$_1$ curve fitted in the range 308-373 K.

Table S6. ^{1}H and ^{7}Li rotational correlation times τ_c (s) calculated for ChCl:U–LiCl(0.8) using the BPP model.

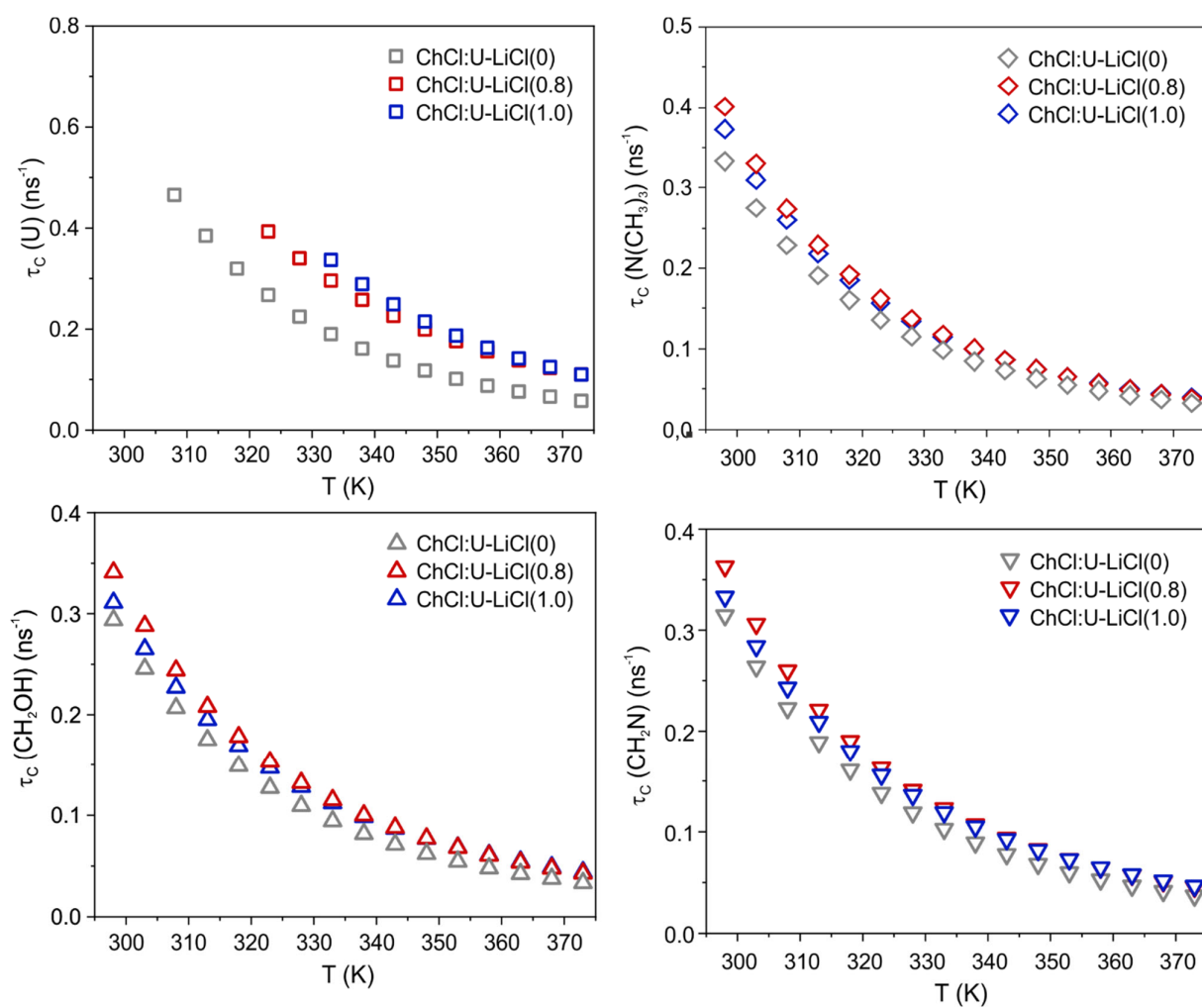| T (K)	U*	CH$_2$OH	CH$_2$N	N(CH$_3$)$_3$	Li
298		$3.41 \cdot 10^{-10}$	$3.63 \cdot 10^{-10}$	$4.01 \cdot 10^{-10}$	$2.97 \cdot 10^{-9}$
303		$2.88 \cdot 10^{-10}$	$3.06 \cdot 10^{-10}$	$3.30 \cdot 10^{-10}$	$2.53 \cdot 10^{-9}$
308		$2.44 \cdot 10^{-10}$	$2.60 \cdot 10^{-10}$	$2.74 \cdot 10^{-10}$	$2.16 \cdot 10^{-9}$
313		$2.08 \cdot 10^{-10}$	$2.21 \cdot 10^{-10}$	$2.29 \cdot 10^{-10}$	$1.86 \cdot 10^{-9}$
318		$1.78 \cdot 10^{-10}$	$1.90 \cdot 10^{-10}$	$1.92 \cdot 10^{-10}$	$1.61 \cdot 10^{-9}$
323	$3.93 \cdot 10^{-10}$	$1.53 \cdot 10^{-10}$	$1.63 \cdot 10^{-10}$	$1.62 \cdot 10^{-10}$	$1.40 \cdot 10^{-9}$
328	$3.40 \cdot 10^{-10}$	$1.32 \cdot 10^{-10}$	$1.41 \cdot 10^{-10}$	$1.37 \cdot 10^{-10}$	$1.22 \cdot 10^{-9}$
333	$2.96 \cdot 10^{-10}$	$1.15 \cdot 10^{-10}$	$1.23 \cdot 10^{-10}$	$1.17 \cdot 10^{-10}$	$1.06 \cdot 10^{-9}$
338	$2.58 \cdot 10^{-10}$	$1.00 \cdot 10^{-10}$	$1.07 \cdot 10^{-10}$	$1.00 \cdot 10^{-10}$	$9.35 \cdot 10^{-10}$
343	$2.26 \cdot 10^{-10}$	$8.79 \cdot 10^{-11}$	$9.39 \cdot 10^{-11}$	$8.63 \cdot 10^{-11}$	$8.25 \cdot 10^{-10}$
348	$1.99 \cdot 10^{-10}$	$7.72 \cdot 10^{-11}$	$8.26 \cdot 10^{-11}$	$7.46 \cdot 10^{-11}$	$7.30 \cdot 10^{-10}$
353	$1.76 \cdot 10^{-10}$	$6.81 \cdot 10^{-11}$	$7.29 \cdot 10^{-11}$	$6.47 \cdot 10^{-11}$	$6.49 \cdot 10^{-10}$
358	$1.56 \cdot 10^{-10}$	$6.03 \cdot 10^{-11}$	$6.45 \cdot 10^{-11}$	$5.64 \cdot 10^{-11}$	$5.78 \cdot 10^{-10}$
363	$1.38 \cdot 10^{-10}$	$5.36 \cdot 10^{-11}$	$5.74 \cdot 10^{-11}$	$4.93 \cdot 10^{-11}$	$5.17 \cdot 10^{-10}$
368	$1.23 \cdot 10^{-10}$	$4.77 \cdot 10^{-11}$	$5.11 \cdot 10^{-11}$	$4.33 \cdot 10^{-11}$	$4.63 \cdot 10^{-10}$
373	$1.10 \cdot 10^{-10}$	$4.27 \cdot 10^{-11}$	$4.57 \cdot 10^{-11}$	$3.81 \cdot 10^{-11}$	$4.17 \cdot 10^{-10}$

* T$_1$ curve fitted in the range 323-373 K.

Table S7. ^{1}H and ^{7}Li rotational correlation times τ_C (s) calculated for ChCl:U-LiCl(1.0) using the BPP model.

T (K)	U*	CH$_2$OH	CH$_2$N	N(CH$_3$)$_3$	Li
298		$3.11 \cdot 10^{-10}$	$3.33 \cdot 10^{-10}$	$3.73 \cdot 10^{-10}$	$2.31 \cdot 10^{-9}$
303		$2.65 \cdot 10^{-10}$	$2.84 \cdot 10^{-10}$	$3.10 \cdot 10^{-10}$	$2.02 \cdot 10^{-9}$
308		$2.27 \cdot 10^{-10}$	$2.43 \cdot 10^{-10}$	$2.60 \cdot 10^{-10}$	$1.77 \cdot 10^{-9}$
313		$1.95 \cdot 10^{-10}$	$2.09 \cdot 10^{-10}$	$2.18 \cdot 10^{-10}$	$1.56 \cdot 10^{-9}$
318		$1.69 \cdot 10^{-10}$	$1.80 \cdot 10^{-10}$	$1.85 \cdot 10^{-10}$	$1.39 \cdot 10^{-9}$
323		$1.47 \cdot 10^{-10}$	$1.56 \cdot 10^{-10}$	$1.57 \cdot 10^{-10}$	$1.23 \cdot 10^{-9}$
328		$1.28 \cdot 10^{-10}$	$1.36 \cdot 10^{-10}$	$1.34 \cdot 10^{-10}$	$1.10 \cdot 10^{-9}$
333	$3.37 \cdot 10^{-10}$	$1.12 \cdot 10^{-10}$	$1.19 \cdot 10^{-10}$	$1.15 \cdot 10^{-10}$	$9.84 \cdot 10^{-10}$
338	$2.89 \cdot 10^{-10}$	$9.84 \cdot 10^{-11}$	$1.05 \cdot 10^{-10}$	$9.94 \cdot 10^{-11}$	$8.84 \cdot 10^{-10}$
343	$2.49 \cdot 10^{-10}$	$8.68 \cdot 10^{-11}$	$9.25 \cdot 10^{-11}$	$8.61 \cdot 10^{-11}$	$7.96 \cdot 10^{-10}$
348	$2.15 \cdot 10^{-10}$	$7.69 \cdot 10^{-11}$	$8.19 \cdot 10^{-11}$	$7.49 \cdot 10^{-11}$	$7.20 \cdot 10^{-10}$
353	$1.87 \cdot 10^{-10}$	$6.83 \cdot 10^{-11}$	$7.27 \cdot 10^{-11}$	$6.54 \cdot 10^{-11}$	$6.52 \cdot 10^{-10}$
358	$1.63 \cdot 10^{-10}$	$6.09 \cdot 10^{-11}$	$6.48 \cdot 10^{-11}$	$5.73 \cdot 10^{-11}$	$5.93 \cdot 10^{-10}$
363	$1.42 \cdot 10^{-10}$	$5.45 \cdot 10^{-11}$	$5.79 \cdot 10^{-11}$	$5.04 \cdot 10^{-11}$	$5.40 \cdot 10^{-10}$
368	$1.25 \cdot 10^{-10}$	$4.89 \cdot 10^{-11}$	$5.19 \cdot 10^{-11}$	$4.45 \cdot 10^{-11}$	$4.94 \cdot 10^{-10}$
373	$1.10 \cdot 10^{-10}$	$4.40 \cdot 10^{-11}$	$4.67 \cdot 10^{-11}$	$3.94 \cdot 10^{-11}$	$4.52 \cdot 10^{-10}$

* T_1 curve fitted in the range 333-373 K.

Figure S4. [1]H correlation time τ_C calculated as a function of temperature in the samples ChCl:U-LiCl(0) (grey), ChCl:U-LiCl(0.8) (red), and ChCl:U-LiCl(1.0) (blue) for U protons (squares, top, left), $N(CH_3)_3$ protons of Ch (diamonds, top, right), CH_2OH protons of Ch (triangles, bottom, left) and CH_2N protons of Ch (inverted triangles, bottom, right).

References

1.   Smith, E.L.; Abbott, A.P.; Ryder, K.S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114*, 11060–11082.

2.   Abranches, D.O.; Martins, M.A.R.; Silva, L.P.; Schaeffer, N.; Pinho, S.P.; Coutinho, J.A.P. Phenolic hydrogen bond donors in the formation of non-ionic deep eutectic solvents: The quest for type v des. *Chem. Commun.* **2019**, *55*, 10253–10256.