Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for

Polarity of Tetraalkylammonium-based ionic liquids and related low temperature molten salts

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Content.

Information to UV/Vis Measurements

The solvent parameters SA, SB, SP and SdP were determined by the solvatochromic method using special solvatochromic dyes (Figure S1).

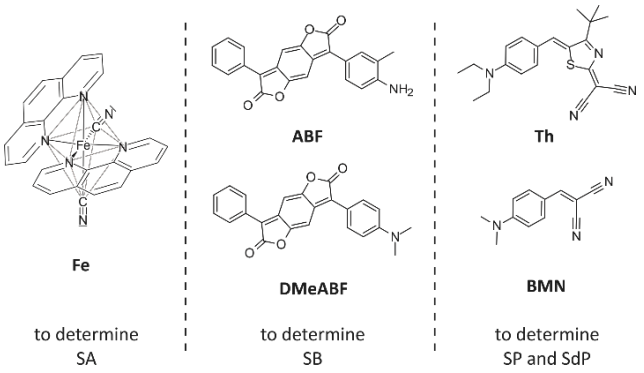

Figure S1. Pairs of solvatochromic dyes, to determine the Catalán parameter SA, SB, SP and SdP of ILs and LTMS. [Fe^{II}(1,10-phenanthroline)$_2$(CN)$_2$] (**Fe**), 3-(4-amino-3-methylphenyl)-7-phenylbenzol[1,2-*b*:4,5-*b'*]difuran-2,6-dione (**ABF**), 3-(4-*N,N*-dimethylaminophenyl)-7-phenylbenzol[1,2-*b*:4,5-*b'*]-difuran-2,6-dione (**DMe-ABF**), 4-*tert*-butyl-2-(dicyanomethylene)-5-[4-(dimethylamino)benzylidene]-Δ^3-thiazoline (**Th**), 2-[4-(*N,N*-dimethylamino)benzylidene]malononitrile (**BMN**)[S1]

Due to the higher SA value of Dichloromethane (DCM) in comparison to [N_{4441}]Cl, it is not possible to determine the SA-Value of the salt in solution, because DCM is the stronger acceptor.[S2] The SB parameter of DCM is smaller than the used salts. However, the SB value of the salts are significantly depending on the concentration (Figure S1). To preserve valid results UV/Vis measurements are performed in the pure salts.

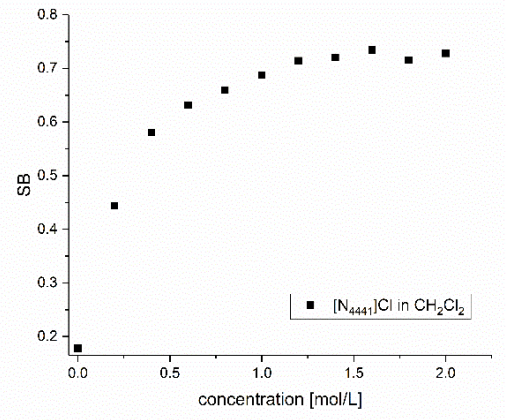

Figure S2 SB parameter of [N_{4441}]Cl as function of the concentration in DCM.

Catalán parameter set [S3,4]

Table S1. Overview of the obtainied UV/Vis spectroscopic data of **Fe**, **ABF**, **DMeABF**, **Th** and **BMN**. a) Due to high temperature the Fe dye was destructed.

substance		$\lambda_{max,Fe}$	$\tilde{\nu}_{max,Fe}$	$\lambda_{max,ABF}$	$\tilde{\nu}_{max,ABF}$	$\lambda_{max,DMeABF}$	$\tilde{\nu}_{max,DMeABF}$	$\lambda_{max,Th}$	$\tilde{\nu}_{max,Th}$	$\lambda_{max,BMN}$	$\tilde{\nu}_{max,BMN}$
cation	anion	[nm]	[*10^{-3} cm^{-1}]	[nm]	[*10^{-3} cm^{-1}]	[nm]	[*10^{-3} cm^{-1}]	[nm]	[*10^{-3} cm^{-1}]	[nm]	[*10^{-3} cm^{-1}]
	Cl	613	16.313	713	14.025	676	14.792	641	15.601	436	22.936
	CF_3CO_2	598	16.722	676	14.793	665	15.037	632	15.823	436	22.936
	Br	a)	/	664	15.060	673	14.858	628	15.923	434	23.041
	NO_3	a)	/	646	15.480	666	15.015	636	15.723	434	23.041
$[N_{4441}]$	$N(CN)_2$	592	16.892	642	15.576	666	15.015	637	15.696	440	22.727
	CF_3SO_3	a)	/	611	16.367	654	15.291	629	15.898	438	22.831
	BF_4	a)	/	596	16.779	653	15.314	627	15.949	432	23.148
	Ntf_2	563	17.762	591	16.920	659	15.175	628	15.924	435	22.989
	PF_6	a)	/	579	17.271	645	15.504	626	15.974	433	23.095
	Cl	607	16.474	724	13.812	674	14.837	630	15.873	432	23.148
	CF_3CO_2	602	16.611	688	14.534	667	14.992	627	15.949	433	23.095
	Br	608	16.447	691	14.471	671	14.903	631	15.848	433	23.095
	NO_3	a)	/	668	14.970	673	14.859	630	15.873	432	23.148
$[N_{8881}]$	$N(CN)_2$	590	16.949	655	15.267	673	14.859	633	15.798	437	22.883
	CF_3SO_3	a)	/	632	15.823	662	15.106	624	16.026	433	23.095
	BF_4	a)		625	16.000	666	15.015	627	15.949	433	23.095
	Ntf_2	587	17.036	608	16.477	664	15.060	626	15.974	436	22.936
	PF_6	a)	/	604	16.556	662	15.106	626	15.974	433	23.095

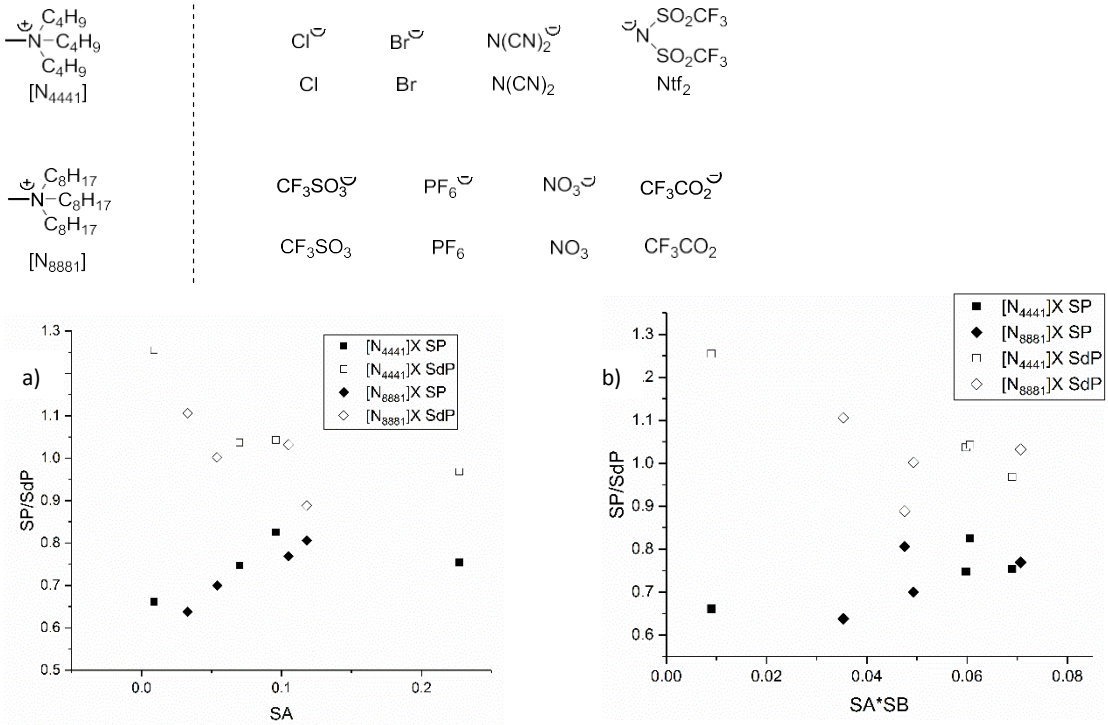

Figure S3 Comparison of SP (filled symbols) and SdP (empty symbols) as function of SA [a)]and SA*SB [b)], respectively, of tri-*n*-alkylmethylammonium cations with various anions.

Kamlet-Taft parameter set

The Kamlet-Taft parameter of IL and LTMS could be calculated with the following equations:[S5,6]

$$\alpha = -7.26 + 0.45\tilde{\nu}_{\max,\mathbf{Fe}}\,[10^3\mathrm{cm}^{-1}]$$

$$\beta = -3.84 + 0.20\tilde{\nu}_{\max,\mathbf{ABF}}\,[10^3\mathrm{cm}^{-1}]$$

$$\pi^* = 9.47 - 0.54\tilde{\nu}_{\max,\mathbf{Th}}\,[10^3\mathrm{cm}^{-1}]$$

Table S2. UV/Vis absorption maxima of the solvatochromic dyes Fe, ABF and Th measured tri-n-alkylmethylammonium salt (according to Scheme 2) and the calculated Kamlet-Taft solvent parameters α, β, π^*.

substance		$\lambda_{\max,\mathbf{Fe}}$	$\lambda_{\max,\mathbf{ABF}}$	$\lambda_{\max,\mathbf{Th}}$	α	β	π*
cation	anion	[nm]	[nm]	[nm]			
	Cl	613	713	641	0.081	1.035	1.046
	CF_3CO_2	598	676	632	0.265	0.881	0.926
	Br	/	/	/	/	/	/
	NO_3	/	646	636	/	0.744	0.979
$[N_{4441}]$	$N(CN)_2$	592	642	637	0.341	0.725	0.993
	CF_3SO_3	/	611	629	/	0.567	0.885
	BF_4	/	596	627	/	0.484	0.858
	Ntf_2	563	591	628	0.733	0.456	0.871
	PF_6	/	579	626	/	0.386	0.844
	Cl	607	724	630	0.154	1.078	0.899
	CF_3CO_2	602	688	627	0.215	0.933	0.858
	Br	/	/	/	/	/	/
	NO_3	/	668	630	/	0.846	0.899
$[N_{8881}]$	$N(CN)_2$	590	655	633	0.367	0.787	0.939
	CF_3SO_3	/	632	624	/	0.675	0.816
	BF_4	604	625	627	/	0.640	0.858
	Ntf_2	587	608	626	0.406	0.551	0.844
	PF_6	/	604	626	/	0529	0.844

^{1}H NMR spectroscopic studies

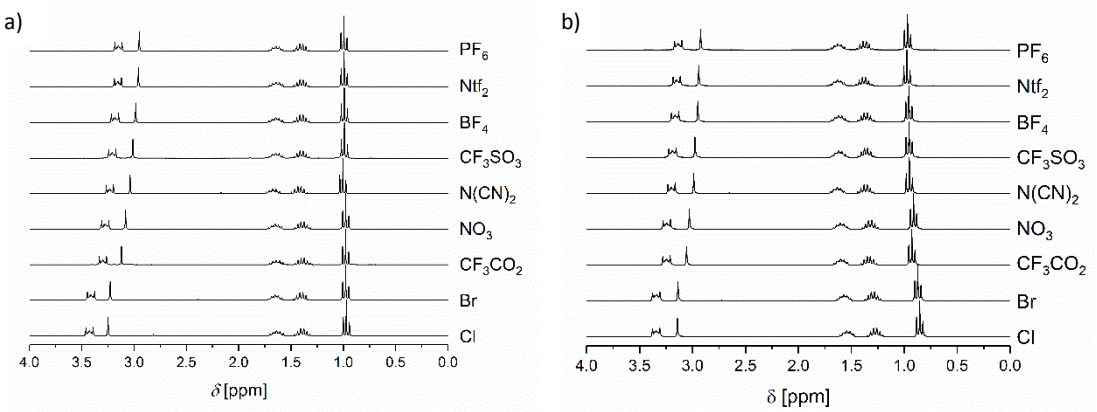

Figure S4 ^{1}H NMR spectra of $[N_{4441}]X$ with various anions in CD_2Cl_2 at the concentration of 0.2 M [a)] and 1.0 M [b)].

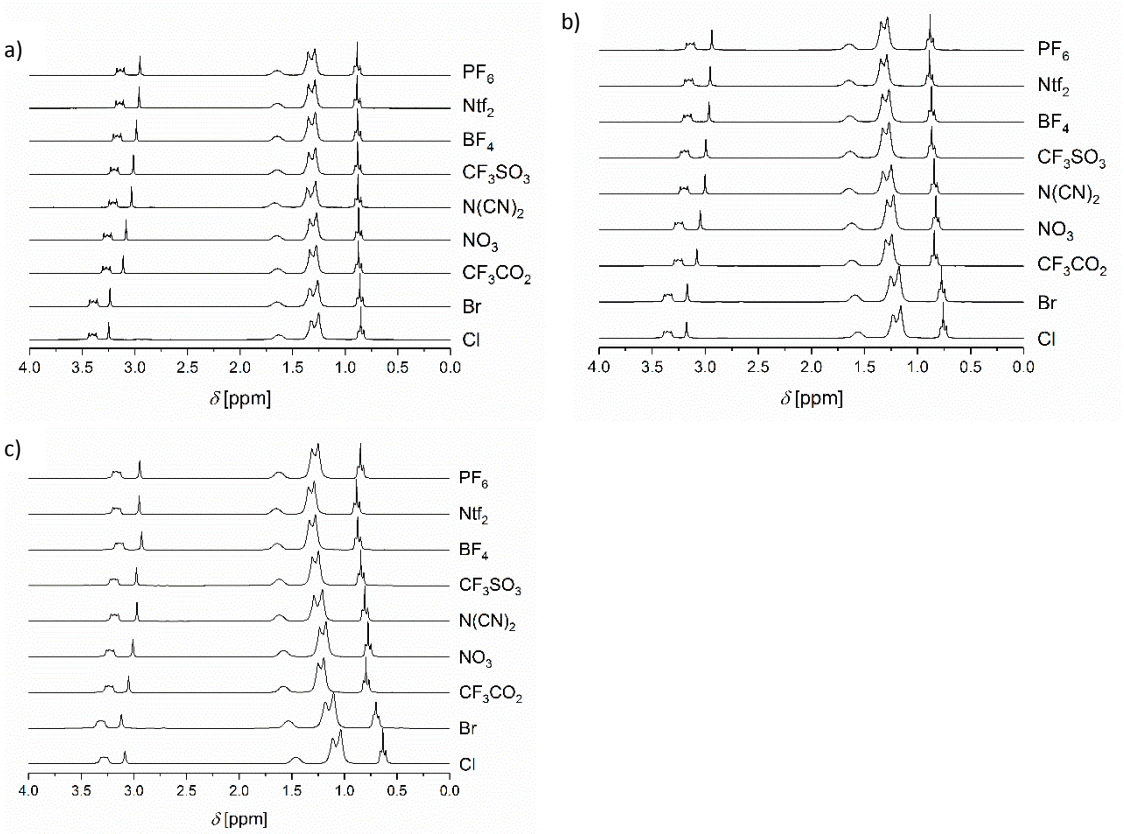

Figure S5 ^{1}H NMR spectra of $[N_{8881}]X$ with various anions in CD_2Cl_2 at the concentration of 0.2 M [a)], 1.0 M [b)] and 1.8 M [c)].

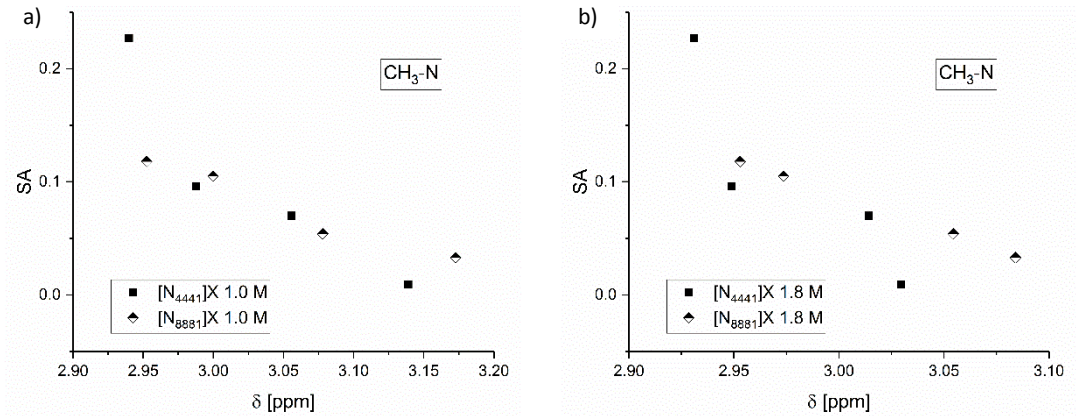

Figure S6 SA as a function of the chemical shift of the hydrogen atoms (CH$_3$-N) measured in CD_2Cl_2 at the concentration of 1.0 M [a)], 1.8 M [b)].

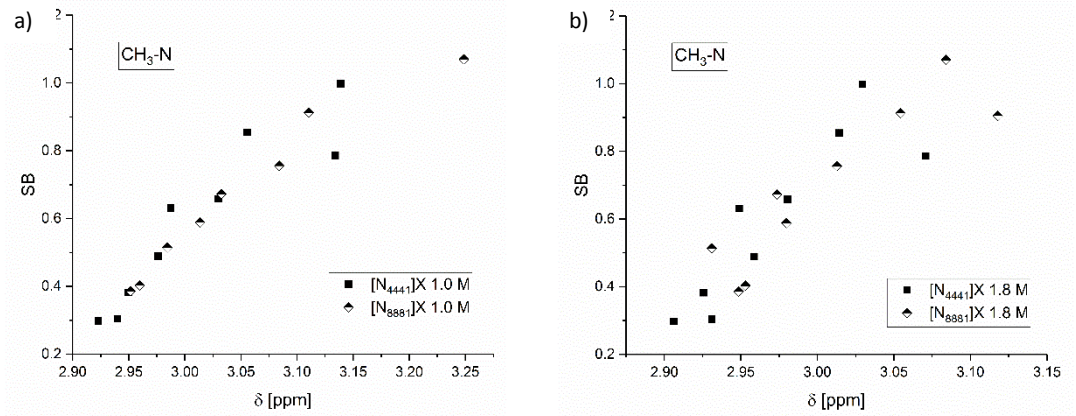

Figure S7 SB as a function of the chemical shift of the hydrogen atoms (CH$_3$-N) measured in CD_2Cl_2 at the concentration of 1.0 M [a)], 1.8 M [b)].

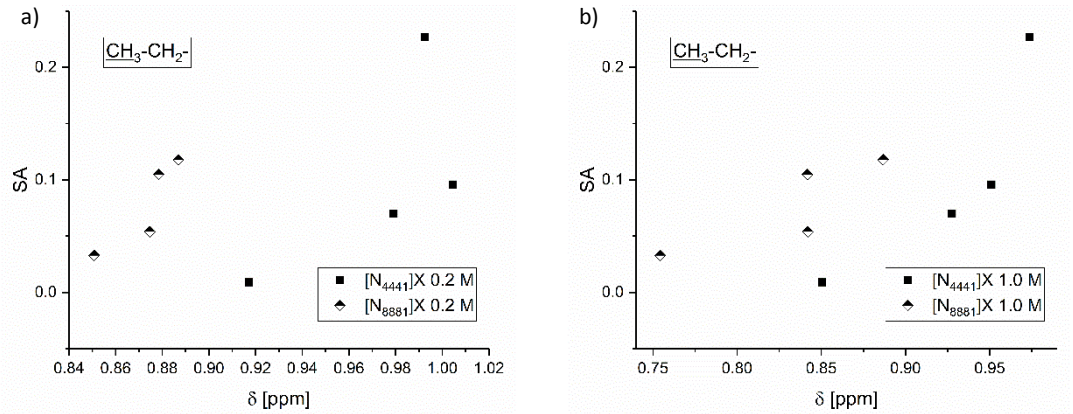

Figure S8 SA as a function of the chemical shift of the hydrogen atoms (CH$_3$-CH$_2$) measured in CD_2Cl_2 at the concentration of 0.2 M [a)], 1.0 M [b)].

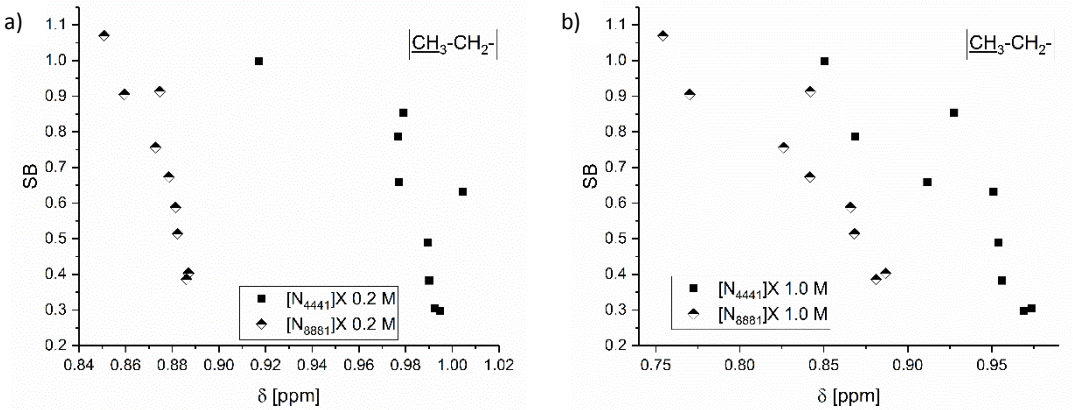

Figure S9 SB as a function of the chemical shift of the hydrogen atoms ($\underline{CH_3}$-CH_2) measured in CD_2Cl_2 at the concentration of 0.2 M [a)], 1.0 M [b)].

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