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Electronic Supplementary Information

For

The influence of the cation structure on the basicity-related polarity of ionic liquids

Nadine Weiß,^a Gabi Thielemann,^a Kevin Nagel,^a Carolin H. Schmidt,^a Andreas Seifert,^a Lysann Kaßner,^a Veronika Strehmel,^b Björn Corzilius,^c Christian Schröder ^d and Stefan Spange *^a

- ^a Department of Polymer Chemistry, Institute of Chemistry, Chemnitz University of Technology, Straße der Nationen 62, 09111 Chemnitz, Germany; E-mail: stefan.spange@chemie.tu-chemnitz.de.
- ^b Department of Chemistry, Organic Chemistry and Institute for Coatings and Surface Chemistry, Hochschule Niederrhein, University of Applied Sciences, Adlerstraße 32, 47798 Krefeld, Germany; E-mail: Veronika.Strehmel@hsnr.de.
- ^c Department of Physical Chemistry, Institute of Chemistry, University Rostock, Dr.-Lorenz-Weg 2, 18059 Rostock, Germany; E-mail: bjoern.corzilius@uni-rostock.de.
- ^d Institute of Computational Biological Chemistry, University of Vienna, Währingerstr. 17, 1090 Vienna, Austria.

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UV/Vis and NMR spectroscopic investigations of the solvatochromic probes FuTCF and ThTCF in ionic liquids

The importance of the purification method and water influence on the result of the UV/Vis measurements along with ¹H NMR studies for **FuTCF** and **ThTCF** are demonstrated in Figs. S1–S10. The ILs purity was checked by measuring the ILs refractive index and comparing it with literature data. It should be emphasized that the ILs high purity must be guaranteed because both dyes **FuTCF** and **ThTCF** are overly sensitive to traces of impurities. The influence of water on UV/Vis spectra of **FuTCF** or **ThTCF** depends on the anion and impurities from hydrolysis reactions as investigated by reference experiments with $[C_4mim]BF_4$.

The ¹H NMR spectra series are shown in Fig. S4-S6, Fig. S8-S10, and corresponding UV/Vis data are depicted in Fig. S1, S2, S3a-c, Fig. S7a-c. However, traces of free fluoride ions also play an essential role in measuring reproducible UV/Vis spectra. For instance, if $[C_4mim]BF_4$ is used as received from the supplier, these disturb the UV/Vis measurement. The **FuTCF**·**F**⁻ adduct is then measured that shows its UV/Vis absorption maximum at $\lambda_{max} = 497 \text{ nm.}^1$ This is also observed despite carefully drying the IL in a vacuum.

$$\mathbf{FuTCF} + \mathbf{BF}_4^- \longrightarrow \mathbf{FuTCF} \cdot \mathbf{F}^- + \mathbf{BF}_3 \tag{S1}$$

The theoretically possible reaction of **FuTCF** with the BF_4^- anion (eq. S1) can be excluded since reference experiments of **FuTCF** with [C₄mim]BF₄ show that this does not occur if traces of fluoride ions have been completely removed (see Fig. S1, ESI). Thus, **FuTCF** can be used as a probe to detect the fluoride-free purity of ILs. Furthermore, water addition does not rapidly hydrolyze the BF_4^- anion within 70 min but split off the pinacol ester B–O bond as demonstrated by ¹H NMR measurement (see Fig. S2, S5, S6, and S10).

Purification of the IL and influence on the UV/Vis spectra of FuTCF and ThTCF

The UV/Vis spectra of **FuTCF** and **ThTCF** measured in as received and purified/dried (over silica gel) $[C_4mim]BF_4$ are shown in Fig. S1. **FuTCF** and **ThTCF** show a clear bathochromic shift in $[C_4mim]BF_4$ when stored over molecular sieve only. The reason for this is to be fluoride ions are present, which could be completely removed by drying and treatment with dried silica gel. In addition, a stronger influence of the fluoride ions on the **FuTCF**- compared to the **ThTCF**-solution can be seen.



Figure S1. UV/Vis spectra of **FuTCF** and **ThTCF** measured in [C₄mim]BF₄; continuous lines: [C₄mim]BF₄ as received from supplier dried over molecular sieve; dashed lines: after carefully purification the IL using the silica method.

Time-dependence of the UV/Vis spectrum of FuTCF in carefully dried [C4mim]BF4



Figure S2. UV/Vis spectra of **FuTCF** measured in $[C_4mim]BF_4$ immediately after dissolution in stoppered cuvette (black line) and after 70 min when exposed to air at room temperature. The water uptake is seen by the broadening of the UV/Vis band at the bottom.

The UV/Vis absorption maximum of **FuTCF** and **ThTCF** in $[C_4mim]BF_4$ at room temperature (25 °C) keep constant in closed cuvettes within a time frame of 70 min.

The slight diffusion of water is indicated by the broadening of the UV/Vis band on both the right and left flank as seen in Fig. S2 and then in Figs. S3a-c and Fig.s 7a-c.

The hydrolytic stability of the **FuTCF**/[C₄mim]BF₄-system as studied by UV/Vis- and ¹H-NMR spectroscopy

UV/Vis spectroscopic investigations

a)

b)





Figure S3a-c. Effect of water addition upon the UV/Vis spectrum of FuTCF dissolved in [C4mim]BF4.

From 60 μ L water addition up to 240 μ L, a bathochromic shift as well as the characteristic of a shoulder can be seen. Reaction product shifts due to the change in polarity of the IL?

¹H NMR spectroscopic investigations

FuTCF is sensitive to water.



Figure S4. ¹H NMR spectra of FuTCF in 0.5 mL DMSO-d₆. Assignment of ¹H signals according to ref. ¹ is given as follows:





Figure S5. ¹H NMR spectra of **FuTCF** in 0.5 mL DMSO-d₆ added with 20 μ L water. The signals a, b for the free pinacol are indicated in the spectrum.



Figure S6. ^1H NMR spectra of FuTCF in 0.5 mL DMSO-d_6 added with 20 μL water after 12.5 hours.

<u>The hydrolytic stability of the ThTCF/[C₄mim]BF₄-system as studied by UV/Vis- and ¹H-NMR spectroscopy</u>

UV/Vis spectroscopic investigations

Same tendencies as in FuTCF can be qualitatively observed.

From 0 to 30 μ L of water addition formation of a longer-waved shoulder and bathochromic shift of the UV/Vis band occurs. From 30 to 90 μ L of added water the intensity of the shoulder decreases. The peak maximum of the UV/Vis band does not shift.

From 90 μL water addition up to 240 μL a bathochromic shift and the characteristic of a shoulder can be seen.



Figure S7a-c. Effect of water addition upon the UV/Vis spectrum of ThTCF dissolved in [C4mim]BF4.

¹H NMR spectroscopic investigations



Figure S8. ¹H NMR spectra of **ThTCF** in 0.5 mL DMSO-d₆. Assignment of ¹H-signals according to ref. ¹ is given as follows:







Figure S9. ¹H NMR spectra of ThTCF in 0.5 mL DMSO-d₆ added with 20 μ L water.



Figure S10. ¹H NMR spectra of ThTCF in 0.5 mL DMSO-d₆ added with 20 μ L water after 20 hours.

The result of broadening and subsequent narrowing of the UV/Vis band with increasing water concentration is likely due to effects of aggregation and de-aggregation. The additional water coordination occurs at the boron atom, resulting in a broader UV/Vs band. At the same time, the pinacol ester bond is hydrolytically cleaved, which makes the situation confusing because different types of free boric acid and ester are present at the same time and overlap (see Fig. S4 and Fig. S8, caption). One also clearly observes a double 1H signal set for the chromophore after the reaction with water after a longer time. Therefore, aggregation may also occur, as is known for free boric acid.² This

aggregation would recede at higher water concentration, which explains the narrowing of the UVV/s band at higher water content and the larger amount of free boronic acid indicated by the signal at 7.6 ppm for FuTCF (Fig. S14). Since no decrease in intensity of the UV/Vis absorption peak is observed, the chromophoric system behaves intact upon water addition.

Conclusion on the influence of water upon stability of the probes: When comparing the ¹H NMR spectra series of **FuTCF** and **ThTCF** it is noticeable that the reaction of water with **FuTCF** is significantly faster than with **ThTCF**.

Importantly, we show that the chromophore is not perturbed by the addition of small portion of water and the UV/Vis peak maximum does not change.

Resume: water content has to be under the detection limit of Karl-Fischer titration. The measurements on air has to be carried out in rush.

UV/Vis spectra of FuTCF, ThTCF and ABF in [C₄mim]Ac

The average of both half width of λ_{max}^* has been used as measure of the absorption energy which corresponds to the centroid wavelength.



Figure S11. UV/Vis spectra of FuTCF (a) and ThTCF (b), respectively, measured in [C₄mim]Ac.



Figure S12. UV/Vis spectrum of **ABF** measured in [C₄mim]Ac. Attend the peak maximum of **ABF** corresponds exactly to the centroid wavelength UV/Vis maximum.



Figure S13. UV/Vis spectra of FuTCF (a) and ThTCF (b), respectively, measured in 12 selected [C4mim]-based ILs.

Evaluation of the UV/Vis absorption band for TCF-containing boronate ester derivatives

The determination of a clear UV/Vis absorption peak maximum for TCF-containing boronate ester derivatives is not always possible because the UV/Vis absorption bands are asymmetric in shapes as seen in Figure S1–S3, S7, S11 and S13 and ref.¹

Therefore, instead of the actual absorption peak maximum, the average of $\lambda_{max,c}^*$, according to equation S1 was used to determine the relevant absorption energy of the UV/Vis absorption band. This methodology has been also used in the previous study, with A absorption intensity.¹

$$\lambda_{\max,C}^* = \left[\lambda(A_{\max}/2)_1 + \lambda(A_{\max}/2)_2\right]/2$$

(S1)

Thus, the average of both half width of λ_{max}^* has been used as measure of the absorption energy. Therefore, discussion of Δv is only possible when significant differences of Δv are observed. $\lambda_{max,C}^*$ of eq. S1 relates to the centroid wavelength which is recommended in the literature^{3,4} for

 $\lambda_{max,C}^*$ of eq. S1 relates to the centroid wavelength which is recommended in the literature^{3,4} for examination of the asymmetric UV/Vis spectrum.



Figure S14. Explanation for determining the centroid wavelength ν_c taken from the ref. 11

Representative UV/Vis spectra of FuTCF and ThTCF in several tetraalkylammonium-based ILs



Figure S15a. UV/Vis spectrum of FuTCF in $[N_{8881}]N(CN)_2$.



Figure S15b. UV/Vis spectrum of FuTCF in $[N_{4441}]N(CN)_2$.



Figure S15c. UV/Vis spectrum of ThTCF in [N₄₄₄₁]N(CN)₂.



Figure S15d. UV/Vis spectrum of ThTCF in [N₄₄₄₁]TFA.

¹¹B NMR measurements

¹¹B NMR spectra were acquired using a spin echo sequence (cpmg1d) to reduce the background signal. Furthermore, all spectra depicted in the next figure are baseline corrected using a blank ¹¹B spectrum obtained from pure solvent, and normalized in intensity.

The dye **ThTCF** in CD_2Cl_2 shows one signal at a chemical shift of 29 ppm (line width about 500 Hz). A broadening of the signal is observed after adding ILs containing nitrate (2), dicyanamide (3), or chloride (4) anions. The line width of the signals increased to more than 1000 Hz indicating nonspecific interactions.

The IL with acetate anion is different showing two signals shortly after adding the IL to the solution of **ThTCF** in CD_2Cl_2 (22.2 ppm; 6.2 ppm), whereas a measurement of the same sample showed only one signal after about one month. Thus, a reaction taking place is more likely rather than physical interactions.



Figure S15. ¹¹B NMR spectra of ThTCF in CD₂Cl₂ /[C₄mim] IL mixtures (see inset).

The IL anion influences the chemical structure of the solvatochromic probe **ThTCF**, which can be monitored by ¹¹B-NMR spectroscopy as the change of sp²-hybridized trigonal boron to the tetrahedral sp³-hybridized boron is associated with a strong up-field shift of the ¹¹B NMR signal. The measurements were carried out in CD_2Cl_2 with a large excess of the IL. For these ¹¹B NMR studies [C_4 mim]CH₃CO₂, nitrate, chloride, and dicyanamide have been used, which show high β and E_{HB} values. The corresponding ¹¹B NMR-spectra are given in the Fig. S16 in the ESI part. The ¹¹B NMR signal of **ThTCF** appears at 28.72 ppm in CD_2Cl_2 . After adding an excess of [C_4 mim]CH₃CO₂, the NMR signal is shifted to 6.52 ppm, which indicates that the acetate anion is covalently coordinated to the boron atom. However, after completing the reaction of ThTCF with acetate, the ¹¹B signal remains at 22 ppm. The UV/Vis spectrum of **ThTCF** is used for immediate evaluation after dissolution and is stable for at least the next 15 min.

The UV/Vis absorbance of $v_{c,max}$ (**ThTCF**)/(C₄mim acetate) at 20 200 cm⁻¹ approaches that of the fluoride adduct of **ThTCF**/(n-C₄H₉)₄N⁺ F⁻ with 19 380 cm⁻¹.¹ For the other ILs, no significant shift of the ¹¹B signal at 28.7 ppm is observed when the IL is added. One observes only a decrease in intensity and significant broadening of the ¹¹B NMR signal. These observations show that the sp²-hybridization of the boron atom at **ThTCF** is not altered by chloride, nitrate, and dicyanamide but is significantly affected by acetate. Nevertheless, the C₄mim ILs with NO₃⁻, Cl⁻ or N(CN)₂⁻ anions exert a strong bathochromic effect on the probe's UV/Vis absorption.

	$\lambda_{\rm c}$ (nm) (\tilde{v}	′ _c (10 ³ cm ^{−1}))			
11	FuTCF	ThTCF	E _{HB}	β(ABF)	
[C₄mim]FAP	432 (23.14)	430 (23.27)	-0,74	0.25	
[C ₆ mim]FAP	423 (23.66)	427 (23.43)	-	0.27	
[C ₄ mim]BF ₄	428(23.34)	428 (23.36)	-9,79	0.55	
[C₀mim]BF₄	439 (22.80)	434 (22.88)	-9,35	0.60	
[C ₈ mim]BF ₄	451 (22.18)	434 (23.04)	-8,99	0.63	
[C ₁₀ mim]BF ₄	461 (21.71)	437 (22.88)	-8,63	0.65	
[C ₄ mim]PF ₆	428 (23.36)	424 (23.58)	-2,88	0.44	
[C ₆ mim]PF ₆	422 (23.68)	422 (23.68)	-2,71	0.50	
[C ₄ mim]N(CN) ₂	479 (20.88)	459 (21.77)	-22,6	0.64	
[C ₆ mim]N(CN) ₂	470 (21.27)	455 (22.00)	-22,05	0.69	
[C ₈ mim]N(CN) ₂	478 (20.93)	450 (22.22)	-21,69	0.71	
[C ₁₀ mim]N(CN) ₂	469 (21.31)	447 (22.39)	-21,2	0.71	
[C ₄ mim]Ntf ₂	431 (23.10)	431 (23.19)	-9,86	0.42	
[C ₆ mim]Ntf ₂	442 (22.63)	435 (23.01)	-9,5	0.44	
[C ₈ mim]Ntf ₂	423 (23.61)	428 (23.39)	-9,22	0.47	
[C ₄ mim]CF ₃ SO ₃	431 (23.21)	429 (23.30)	-17,11	0.57	
[C ₆ mim]CF ₃ SO ₃	456 (21.92)	438 (22.82)	-16,63	0.61	
[C ₈ mim]CF ₃ SO ₃	437 (22.88)	439 (22.76)	-16,26	0.64	
[C ₆ mim]Br	454 (22.02)	447 (22.38)	-	0.88	
[C ₈ mim]Br	451 (22.20)	447 (22.36)	-	0.89	
[C ₁₀ mim]Br	444 (22.51)	446 (22.44)	-	0.91	
[C ₄ mim]Cl	456 (21.90)	451 (22.18)	-30,72	0.95	
[C₀mim]Cl	471 (21.24)	456 (21.92)	-30,11	0.97	
[C ₁₀ mim]Cl	466 (21.48)	453 (22.06)	-29,18	0.98	
[C ₄ mim]NO ₃	463 (21.60)	449 (22.27)	-24,21	0.74	
[C ₆ mim]NO₃	452 (22.12)	441 (22.65)	-23,58	0.76	
[C ₄ mim]CF ₃ CO ₂	463 (21.60)	448 (22.30)	-24,38	0.74	
[C₄mim]OctOSO	435 (22.97)	434 (22.88)	-20,76	0.77	
3					
[C ₄ mim]ClO ₄	424 (23.57)	425 (23.54)	-13,11	0.55	
[C ₄ mim]CH ₃ CO ₂	488 (20.49)	495 (20.20)	-40,17	0.88	

Tables with results for 1,3-dialkylimidazolium- and tetraalkylammonium-based ionic liquids

Table S1. Compilation of measured centroid wavelengths λ_c and $\tilde{\nu}_c$ of **FuTCF** and **ThTCF** in various ionic liquids *and* the Freire E_{HB} parameter (ref. 5) of the IL.

Table S2 A_{iso} data of spin probes, UV/Vis data of **ThTCF** and **FuTCF**, solvatochromic KAT parameters and molar concentrations (N) for several 1,3-dialkylimidazolium-based ionic liquids at 25°C; references see footnotes.

		A _{iso} (¹⁴ N) [G]	A _{iso} (¹⁴ N) [G]	A _{iso} (¹⁴ N) [G]						
	E (20)	он Д	– <mark>N</mark> ⊕⊖I	∋ O [⊖] K [⊕] I O=S=O		0	_* .	v_{max} (10 ³ cm ⁻¹)		N (mol/cm ³)
	E _T (30)	√N V V	N V V		a	p	π	FuTCF	ThTCF	
		TEMPOL	KATION	ANION						
[C₃mim]N(Tf)₂	51.9	15.84	15.77	16.08	-	-	-	_	_	_
[C ₄ mim]N(Tf) ₂	51.7	15.98	15.81	16.15	0.55	0.42	0.83	23.10	23.20	0.00343
[C ₆ mim]N(Tf) ₂	51.7	15.81	15.74	16.76	0.51	0.44	0.86	22.63	23.01	0.00306
[C ₈ mim]N(Tf) ₂	51.4	15.94	15.87	16.94	0.48	0.47	0.86	23.61	23.39	0.00269
[C ₁₀ mim]N(Tf) ₂	51.0	15.81	15.84	16.90	0.48	0.49	0.86	_	_	0.00253
[C ₄ mim]BF ₄	52.4	15.8	15.68	15.98	0.52	0.55	0.96	23.34	23.36	0.00531
[C ₆ mim]BF ₄	53.6	15.8	15.49	16.08	0.44	0.60	0.96	22.80	22.88	0.00451
[C ₈ mim]BF ₄	51.9	16.0	14.23	16.25	0.45	0.63	0.93	22.18	23.04	0.00392
[C ₁₀ mim]BF ₄	-	15.8	14.06	16.25	0.47	0.65	0.90	21.71	22.88	0.00345
[C₄mim]PF ₆	52.6	15.8	14.89	16.04	0.54	0.44	0.90	23.36	23.58	0.00480
[C ₆ mim]PF ₆	52.3	15.8	13.71	16.05	0.51	0.50	0.96	23.68	23.68	0.00416
[C ₈ mim]PF ₆	50.1	15.8	13.73	16.15	0.52	0.53	0.92	23.34	23.36	0.00339
[C ₁₀ mim]PF ₆		15.9	13.15	16.15	0.48	0.55	0.89	_	_	0.00325
[C ₄ mim]N(CN) ₂	51.5	_	15.74	15.94	0.44	0.64	0.98	20.88	21.77	0.00516
[C ₆ mim]N(CN) ₂	51.0	_	15.53	16.05	0.44	0.69	1.00	21.27	22.00	0.00446
[C ₈ mim]N(CN) ₂	_	_	15.67	16.28	0.43	0.71	0.97	20.93	22.22	0.00388
[C ₁₀ mim]N(CN) ₂	-	_	15.57	16.42	0.44	0.71	0.96	21.31	22.39	0.00347
[C ₄ mim]CF ₃ SO ₃	52.1	15.77	15.60	16.22	0.50	0.56	0.90	23.21	23.30	0.00453
[C ₈ mim]CF ₃ SO ₃	-	15.98	14.86	16.66	0.50	0.63	0.89	22.88	22.76	0.00332
[C ₂ mim]FAP	51.6	15.98	15.88	16.25	0.83	0.20	0.83	_	_	0.00308

 $E_T(30)$ parameters are from ref. 6, $E_T(30)$ for $[C_3mim]N(Tf)_2$ is from ref.⁷.

KAT parameters are in part from ref.⁸ and ⁹, A_{iso} values are in part from ref ¹⁰⁻¹³.

N values are from ref. ¹⁴⁻¹⁵. *N* for C₂mimFAP was newly calculated from the density 1.715 g/cm³ (ref. ¹⁶) M = 556.174 g/mol.

Table S3 ¹⁴N isotropic hyperfine coupling constants (A_{iso}) of the two spin probes CATI and TSKCr measured in various tetraalkylammonium-based ILs and corresponding empirical KAT polarity parameters, as well as the UV/Vis data of **FuTCF** and **ThTCF**.

IL	A _{iso} (¹⁴ N)/G (CATI)	A _{iso} (¹⁴N)/G (TSKCr)		β	π* -	ν _{max} (10 ³ cm ⁻¹)	
			α			FuTCF	ThTCF
[N ₄₄₄₁]N(CN) ₂	15.8	17.4	0.25	0.73	0.99	n.r.	22.67
[N ₄₄₄₁]NTf ₂	16.1	17.6	0.41	0.46	0.87	23.3	23.25
[N ₄₄₄₁]CF ₃ CO ₂	n.i.	17.1	0.265	0.88	0.88	21.8	22,34
[N ₆₆₆₁]N(CN) ₂	15.8	17.7	0.24	0.8	0.96	n.r.	22.42
[N ₆₆₆₁]NTf ₂	16.5	17.8	0.7	0.51	0.9	22.8	22.84
[N ₆₆₆₁]CF ₃ CO ₂	n.i.	17.5	n.d	0.76	0.9	n.r.	_
[N ₈₈₈₁]N(CN) ₂	15.2	17.7	0.25	0.79	0.94	n.r	22.4
[N ₈₈₈₁]NTf ₂	15.6	17.5	0.39	0.55	0.85	23.01	23.01
[N ₈₈₈₁]CF ₃ CO ₂	n.i.	17.5	0.23	0.93	0.86	n.r.	21.9
[N ₁₀₁₀₁₀₁]N(CN) ₂	15.0	17.4	n.d.	0.82	0.91	n.r.	22.32
[N ₁₀₁₀₁₀₁]NTf ₂	15.6	17.1	n.d.	0.57	0.86	22.9	22.77
[N ₁₀₁₀₁₀₁]CF ₃ CO ₂	n.i.	17.3	n.d.	0.95	0.86	n.r.	22.2

n.i. – not isotropic

n.d. - not determinable due to insolubility of Fe(phen)₂(CN)₂

n.r. – not reliable, because a shoulder appears which is not utilizable.

KAT values are calculated partly from the UV/Vis data from the SI part of ref.⁹

anion	DN	N (mol/cm³)	Ref.
FAP	-12.3	0.00308	16
N(Tf) ₂	11.2	0.00388	15
CF_3SO_3	20.4	0.00532	15
(Et ₂ O)PO ₂	31.3	0.00437	22
N(CN) ₂	37.8	0.00622	15
Ac	43.3	0.0065	15
SCN	45.9	0.00659	15
EtOSO ₃	22.3	0.00524	15
C(CN) ₃	26.1	0.00537	20
NO ₃	22.2	0.0074	15
CIO ₄	7.6	0.00637	21
BF ₄	7.3	0.00634	15
PF ₆	-6.2	0.0055	15
Cl	72.7	0.00809	15
Br	76.7	0.00775	15
B(CN) ₄	20.3	0.00558	15

Table S4 Donor numbers (*DN*) of $[C_2 mim]$ -based ILs from the ref.¹⁸ and *N* values from V_m of ref.¹⁵ and newly calculated *N* from density data (25°C) from different literature references.

For several ILs from ref. ¹⁸ as for example C_2 mim methoxyacetate (CH₃OCH₂CO₂) it was impossible to find experimentally determined density values.





Figure S17. ESR spectra of CATI in the tetraalkylammonium-based ILs $[N_{4441}]DCA$, $[N_{4441}]N(Tf)_2$, $[N_{4441}]TFA$, $[N_{6661}]DCA$, $[N_{6661}]N(Tf)_2$, $[N_{6661}]TFA$, $[N_{8881}]DCA$, $[N_{8881}]N(Tf)_2$, $[N_{1010101}]DCA$, $[N_{1010101}]N(Tf)_2$, $[N_{1010101}]TFA$ measured at room temperature.



Figure S18. ESR spectra of TSKCr in the tetraalkylammonium-based ILs $[N_{4441}]DCA$, $[N_{4441}]N(Tf)_2$, $[N_{4441}]TFA$, $[N_{6661}]DCA$, $[N_{6661}]N(Tf)_2$, $[N_{6661}]TFA$, $[N_{8881}]DCA$, $[N_{8881}]N(Tf)_2$, $[N_{1010101}]DCA$, $[N_{1010101}]N(Tf)_2$, $[N_{1010101}]TFA$ measured at room temperature.

Correlations of various polarity parameter with A_{iso}

1. Correlation of v_{max} (FuTCF) with A_{iso} (TSKCr) and A_{iso} (CATI) of 1,3-dialkylimidazolium-based ILs





Figure S19. Correlation of v_{max} (**FuTCF**) as a function of a) A_{iso} (anionic) (above) and b) A_{iso} (cationic) (below) for 1-alkyl-3-methylimidazolium-based ILs.

2. Aspects on tetraalkylammonium ILs regarding correlations of A_{iso} with UV/Vis data of probes

The graphs plotting A_{iso} values as a function of alkyl chain length for several tetraalkylammonium-based ILs are shown in the following Fig. S20.



Figure S20. Dependencies of A_{iso} (TSKCr) and A_{iso} (CATI) as a function of alkyl chain length (n) of $(C_nH_{2n-1})_3N$ -CH₃ cations. Results from cationic spin probe (filled symbols) and anionic spin probe (empty symbols).

 A_{iso} (CATI) values initially increase with increasing chain length, demonstrating that the interaction between anion and spin probe also increases, but only up to a chain length of six carbon atoms. Then, A_{iso} decreases again, regardless of whether the A_{iso} value of anionic or

cationic spin probe is considered. These results prove that the effect of the anion on A_{iso} seems independent of both the cation structure and charge of the spin probe used.

3. Correlation of v_{max} (ThTCF) with A_{iso} (TSKCr)



Figure S21. Plotting of v_{max} (ThTCF) as a function of A_{iso} (TSKCr) for tetraalkylammonium-based ILs.



4. Correlation of β with A_{iso} (CATI)

Figure S22a. Correlation of β with A_{iso} (CATI) for tetraalkylammonium-based ILs.

5. Correlation of β with A_{iso} (TSKCr)



Figure S22b. Correlation of β with the anionic spin probe A_{iso} (TSKCr) for tetraalkylammonium-based ILs.

6. Correlation of π^* with A_{iso} (CATI) and A_{iso} (TSKCr).

For the cationic spin probe, separate linear plots of π^* as a function of A_{iso} (CATI) are recognizable (Fig. S23a) for the tetraalkylammonium-based ILs. A_{iso} increases with the growing IL dipolarity/polarizability regardless of whether N(Tf)₂ or N(CN)₂ are used. A related result is found for the anionic spin probe (see Fig. S23b in ESI), but the linearity for each anion family is not so obvious.



Fig. S23a Relationships of π^* as a function of A_{iso} (CATI) for tetraalkylammonium-based ILs.

Other anions such as BF_4 or chloride, which have opposite properties in terms of their oxidation potential and HBA-ability, are not possible for tetraalkylammonium ions because these compounds are solid at room temperature.¹⁴

We would like to emphasise that for $N(Tf)_2$ -containing tetraalkylammonium ILs, in comparison to $N(CN)_2$ -containing ILs, no opposing plots are observed, regardless of whether a cationic or anionic spin probe is used, in contrast to the imidazolium-based ILs.



Figure S23b. Correlation of π^* with A_{iso} (TSKCr) for tetraalkylammonium-based ILs.

7. Correlation E_T (30) and α vs. A_{iso} (TEMPOL)



Figure S24a. Plotting of $E_{T}(30)$ as a function of A_{iso} for TEMPOL dissolved in imidazolium-based ILs.



Figure S24b. Correlation of α as a function of TEMPOL for 1-alkyl-3-methylimidazolium-based ILs.



Evaluation of β (ABF) and β (NA) values from literature with respect to V_m or N

Fig. S25 Correlation of β (ABF) (ref. ⁸) for each specific anion as a function of the molar volume of the corresponding cation, V_m data are taken in part from ref.¹⁵ Attend, the β values for [C_xmim]N(Tf)₂ ILs (black filled triangel) in this figure were determined by the 4-nitroaniline/4-*N*,*N*-diethylaminonitroaniline solvatochromic pair and taken from the ref. ⁵.



Figure S26. Plotting β (derived from 4-nitroaniline) as a function of *N* for monoquaternized 1,4-diazobicyclo[2.2.2]octane (dabco) dicyanamide anion ILs, both β and *N* were taken from ref.¹⁷

Results of quantum-mechanical calculations

In our previous study¹⁴ we computed the polarizabilities and dipole moments of various cations and anions employing MP2/6-31+G(d) using Psi4. As the ions are charged species, a reference site for the computation of the dipole moment has to be stated which is the center-of-mass in our case. For the optimized geometry, also the energy of the HOMO and LUMO are obtained. The latter is often

used to characterize the electron affinity.

Both quantities, the LUMO energy and the dipole moment, are shown in Fig. S27 for the imidazoliums with increasing chain length. As visible, the electron affinity is almost constant as a function of the alkyl chain length since the imidazolium ring should play the most important role for that property.



Figure S27 a) LUMO energies of imidazolium cations as a function of the alkyl chain length; b) Dipole moment with respect to the center-of-mass for the same cations.

The increase in β as a function of V_m is a clear indication of increasing the dipolarity/polarizability (molar polarizability) portion according to the theory (ref. ¹⁴) as shown in correspondence to increase of dipole moment of the cation according to Fig. S27b.



Correlation of the Donor number (DN) of ILs from ref. 18,19 with N



DN = 14966 *N* - 54.606 *n* = 8, *r* = 0.976, *sd* = 4.130

Fig. S29 Plotting *DN* (ILs from ref.¹⁸) as a function of *N* for $[C_2mim]$ -based ILs including all data from tab. S4. C_2mim (Et₂O)PO₂ was not considered because it does not fit at all.

/F+ 0100

Fig. S28 Correlation of *DN* (only ILs from ref.¹⁹) as a function of *N* for $[C_2mim]$ -based ILs including FAP, N(Tf)₂, triflate, Ac, dicyanamide, SCN, ethylsulfate and tricyanomethide.



Fig. S30 Plot of Laurence β_1 value ²³ as a function of *N*.

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